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FOREWORD

This technical session was sponsored jointly by the Cane Sugar Refining Research Project, Inc., and the Southern Regional Research Center, U.S. Department of Agriculture. The program was arranged by Dr. Margaret A. Clarke and Dr. Frank G. Carpenter. The conference coordinator was Shirley T. Saucier.

This is one of a series of technical sessions held every other year to provide for an exchange of information among technical leaders in the cane sugar industry, and to report on research and recent developments of benefit to the cane sugar refining industry.

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DEXTRAN PROBLEMS IN SUGAR REFINING: A CRITICAL LABORATORY EVALUATION

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INTRODUCTION

Increasing awareness of dextran-induced problems in the manufacture of cane sugar has led to the development of methods for measuring the dextran content of cane juice and raw sugar. The Nicholson and Horsley Method (Nicholson and Horsley 1959), subsequently slightly modified by Keniry, Lee, and Mahoney (1969), is based on the haze developed in 50% ethanol following elimination of interfering inorganic salts by use of ion exchange resin, precipitation of proteinaceous compounds by trichloroacetic acid and enzymatic removal of the starch. This haze procedure, considered to be one of the best and the most practical methods for dextran determination, was recommended to the 16th session of ICUMSA (1974) for consideration and was tentatively adapted as the official method of dextran analysis for raw sugar at the 17th session of ICUMSA (1978).

In this paper, the ICUMSA haze method is re-examined in detail to ensure the reliability and reproducibility of the test. The subsequent revised method was used as one of the tools in assessing and quantifying the extent to which high dextran raw sugars affect the refining performance.

The report represents part of the findings of our investigation into dextran-induced problems initiated following a series of severe difficulties experienced by our refineries in processing high dextran raw sugar during early 1978 (Hanson 1980).

ANALYTICAL PROCEDURE

Effect of the Alcohol vs. Water Ratio on Haze Formation

It has been cited many times in the literature, that depending on the type of dextran, haze formation commences at an ethanol strength of about 35%, and is usually completed at 42 to 45%. Extending the concentration to 50% ensures that dextran has been quantitatively precipitated.

The nature and proportion of this ethanol to water ratio was studied in regard to its effect on the dextran haze formation. This was done in light of the various grades of reagent ethanol available, the effect of a change in the partial molar volume of ethanol, and effective ethanol concentration.

Table 1.--Effect of anhydrous denatured alcohol on absorbance

Concentration of dextran soln. T-40, mg/25ml.	Cell length cm	Absorbance @ 720 nm* anhydrous alcohol	
		200 proof	denatured 200 proof
2.0	2	.157	.162
3.0	2	.287	.293
4.0	2	.410	.408

* Average of 2 determinations.

The effect of solids present in the aqueous solution, the cell lengths and the order of ethanol addition on haze measurements was also studied.

The cell length and order of addition of ethanol were found to have no significant effect on the final results. However, the solids content in the filtrate cause variation in the results for some raw sugars. The experimental details are listed in appendix 1.

Comparison of 200 Proof Anhydrous Alcohol vs. 200 Proof Denatured Alcohol on Haze Formation. An intra-laboratory experiment was performed in which a number of pure dextran solutions (T-40 M.W.) of varying concentrations were prepared in duplicate. One set was quantitatively precipitated by the addition of 200 proof anhydrous enthanol, the other with 200 proof anhydrous denatured ethanol (Baker's Alcohol Anhydrous Code 3-9401).

It can be seen from the results shown in Table 1 that the net absorbances, measured for duplicate samples produced by the addition of the two different ethanols used, were essentially the same. The differences between readings were well within $\pm$ 5%.

It should be pointed out that different types of denaturing agents used by manufacturers may affect the extent of haze formation.

Comparison of 200 Proof Anhydrous Denatured Alcohol vs. 190-Proof Denatured Alcohol on Dextran Haze Formation. Finding no influence of the denaturing agents in the 200 proof ethanol used on the amount of dextran haze formed, led next to the study of the effect of ethanol with respect to its water content on dextran precipitation.

Again an intra-laboratory experiment was designed in which a number of pure dextran solutions (T-40 M.W.) of varying concentrations were prepared in duplicate. In set No. 1 the dextran was precipitated by the addition of 200 proof anhydrous ethanol, set No. 2 with 190 proof ethanol.

The results of this experiment (Table 2) show a significant decrease in the amount of haze formed in the solutions

Table 2.--Effect of denatured 190 proof alcohol on absorbance

Concentration of dextran soln. T-40, mg/25ml.	Absorbance @ 720 nm*		Average % Diff.
	Anhydrous denatured 200 proof	denatured 200 proof	
2.0	.162	.076	53.1
3.0	.293	.146	50.2
4.0	.408	.230	43.6

* 2 cm cell; average of 2 determinations

precipitated by the 190 proof ethanol, when compared to the 200 proof ethanol. This lowering of measured absorbances (approximately 50%) in the 190 proof samples was due to a decrease in the effective alcohol concentration by the water content. In other words, the water content drops the ethanol concentration into the critical limits needed for complete dextran precipitation as previously mentioned. In view of this a specific grade of reagent ethanol must be employed at all times in order to produce uniform analytical results.

Effect of a Change in the Partial Molar Volume of Alcohol on Dextran Haze Formation. The volume of an ideal solution is simply the sum of the volumes of the components. This is not true for many real solutions, as in the case of the dextran haze solution. When 12.5 mls. of ethanol are added to 12.5 mls. of water, the resulting solution does not occupy 25 mls. but less. This property is defined in terms of partial molar volumes.

Since the partial molar volume of ethanol in water plays an important part in the development of the dextran haze, as shown in the above section, an experiment was designed to determine the effect of a slight change in this quantity on the haze measurement.

12.5 ml. each of pure dextran solutions of varying concentration were micropipeted into two sets of 25 ml. volumetric flasks. One set of the dextran solutions was quantitatively precipitated by the addition of 190 proof ethanol to the marks on the flasks (approximately 13.5 ml. was needed). The other set was precipitated by the addition of 12.5 ml. aliquots of 190 proof ethanol.

As shown in Table 3, the resulting absorbances measured for the dextran solutions precipitated with exactly 12.5 ml. of ethanol were 45% lower than those precipitated by addition of the ethanol to the mark (25 ml.).

As in the case of the previous experiment comparing 200 versus 190 proof ethanol, the effective ethanol concentration was lowered below the critical limit needed for total quantitative precipitation of the dextran. The need for strict adherence to the analytical procedure was further stressed if reproducible and accurate experimental measurements are to be achieved.

Table 3.--Effect of alcohol volume on absorbance (190 proof)

Concentration of dextran soln. T-40, mg/25ml.	Absorbance @ 720 nm*		Average % diff.
	12.5 ml sample + alcohol to 25 ml vol.	12.5 ml sample + 12.5 ml of alcohol	
0.6 (10 cm cell)	.044	.021	52.3
2.0 (5 cm cell)	.208	.106	49.0
4.0 (1 cm cell)	.111	.067	39.6

* Average of 2 determinations

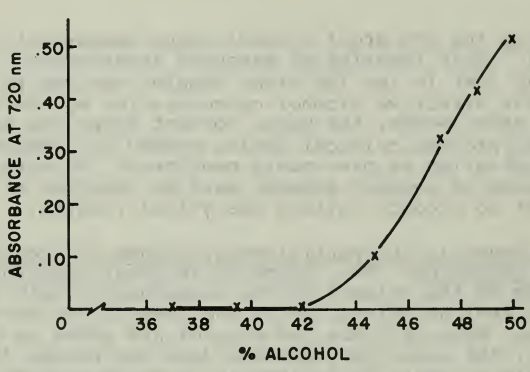


Figure 1.--Turbidity developed as a function of alcohol concentration.

Effect of Alcohol Concentration on the Initiation and Completion of Dextran Precipitation. Viewing the results compiled in the previously described experiments, prompted us to reexamine the figures quoted for commencement and completion of dextran precipitation specifically for T-40 molecular weight dextran.

Literature results quote an initiation of precipitation at approximately 35% ethanol and completion at about 42 to 45%. These figures did not exactly correlate with our findings in the 190 proof ethanol experiments.

In order to resolve this difficulty, an experiment was conducted in which seven ethanol solutions of varying proofs were prepared from 200 proof anhydrous stock ethanol. The concentrations of the ethanols were as follows: 150, 160, 170, 180, 190, 195 and 200 proof respectively. Seven samples containing the same dextran concentration (5 mg./25 ml.) were prepared according to the procedure. Each sample in turn was precipitated with varying strength ethanols. This resulted in a range of ethanol concentrations in the flasks of approximately 37 to 50%.

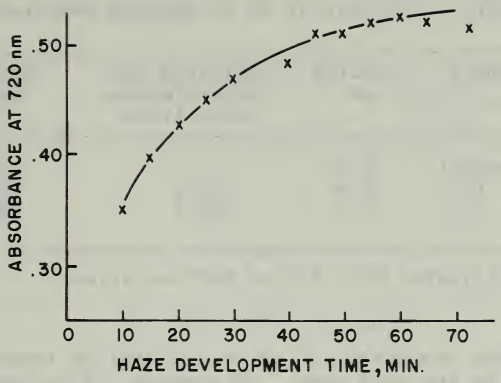


Figure 2.--Effect of haze development time on absorbance for T-40 dextran.

The results of the experiment showed that precipitation commenced between 42 and 45% and was not yet complete at 48%. A graphical representation of these results can be seen in Figure 1.

Again it becomes apparent that the strictest attention must be paid to the alcohol addition part of the dextran procedure in order to maintain reproducibility of measurements.

The Effect of Time on Dextran Haze Development

Although the factor of the effect of time on dextran haze development has been studied by other researchers, specifically CSRRP in Technical Report No. 46, we deemed it necessary to re-examine this parameter in more detail to further stress its importance.

For the experiment, a standard T-40 M.W. dextran solution of 5 mgs. concentration and 200 proof anhydrous ethanol was used. The effect of time of haze development was plotted in Figure 2.

Viewing the curve it becomes immediately obvious why the 60 minute development time is recommended over the previous 20 minute interval. Notice that the 20 min. interval intersects the curve at its steepest portion, where a five minute deviation in haze measurement can mean as much as 20% difference in measured absorbance. On the other hand, in the region of 60 minutes a five minute deviation results in differences in the magnitude of only 2% giving a better reproducibility for the method.

Effect of pH on Dextran Haze Measurement

In the evaluation of dextran removal by clarification processes, including phosphatation and carbonation, it was initially found that the dextran content of liquor after processing was higher than that of liquor before clarification. The possible cause of this seemingly contradictory result was investigated in some detail.

Table 4.--Effect of pH on dextran measurements

Sample	Initial pH	Adjusted pH* before enzyme hydrolysis	Dextran ppm
control	5.9	-	121
1	5.9	8.2	132
2	5.9	10.2	236

* Adjusted with dilute NaOH solution.

Table 4 shows the effect of pH on the dextran concentration as determined by the haze test. In summary, it was concluded that a high pH deactivates the enzyme used for removal of the starch before haze measurement. This incomplete removal of starch contributes to haze formation resulting in a higher amount of dextran in the determination.

In view of this finding, a recommended precaution is to adjust all samples before beginning dextran analysis so that their pH fall within the limits of 5.5 to 6.5 pH. This is the optimal operating range for the particular enzyme employed for starch hydrolysis.

Other study related to the subject of pH is presented in Appendix 2.

Reproducibility of Dextran Analysis by the Modified Haze Method

After studying the approach, technique and chemistry of the Modified Haze Method in detail, the next step is to evaluate its worth by examining its reproducibility.

This evaluation is divided into three sections: (A) recovery of dextran from spiked samples, (B) reproducibility of results between analysts in the same laboratory for unknown raw sugar samples and (C) reproducibility of results for raw sugar samples among a number of outside laboratories.

Recovery of Standard T-40 M.W. Dextran from Spiked Sugar Samples. In this experiment, three samples for dextran analysis by the Modified Haze Method were prepared from a white granulated sugar (premium grade). Two samples were spiked with known additions of T-40 dextran in the amounts of 1020 and 511 ppm., respectively. The third sample was maintained as a blank. The three samples were then analyzed for dextran. The results in ppm. for the two spiked samples are listed in Table 5.

From the results it can be seen that in both cases all of the dextran was accounted for within $\pm$ 2%.

Intra-Laboratory Reproducibility of Dextran Determinations for Raw Sugars. Having been encouraged by the recovery of T-40 standard dextran from spiked samples, an intra-laboratory experiment was conducted. Three raw sugar samples were selected from varying origins and analyzed for dextran by two

Table 5.--Recovery of dextran T-40 added to sugar samples

Dextran added ppm	Absorbance @ 720 nm	Dextran recovered ppm
none	.001	none
511	.085	524
1020	.235	1000

Table 6.--Intra-laboratory reproducibility of dextran measurements

Sample code #	Dextran, ppm		% difference
	Analyst 1	Analyst 2	
68	941	969	3.0
78	1545	1540	~0
89	337	331	~0

different analysts. Again the Modified Haze Method was employed in the analysis, the detailed results of which are listed in Table 6.

As can be seen from viewing the results, the reproducibility of these tests appears extremely good. However, reproducibility of this sort for the "haze method" has been reported in the past. For example, Richards and Stokie (1974) in "Analysis of Dextran in Sugar--An Enzymatic Method" show that differences between duplicate determinations by the haze method varied from zero to 5.6%.

Reproducibility of the Modified Haze Procedure. An Inter-Laboratory Study. In light of the previous results, the next step was to evaluate the reproducibility of the procedure among a number of different Laboratories.

Four of our affiliated laboratories and one independent laboratory were chosen for this collaborative study. Again three samples of raw sugar were selected. These samples were analyzed for dextran by our laboratory and also by each of the five different laboratories. The results of these tests are listed in Table 7.

Aside from the results obtained from laboratory No. 2 for samples 68 and 78, the reaminder of the test results fall within expected experimental error. The deviation from the norm by laboratory No. 2 is yet to be investigated.

Standard Dextran Reference

The influence of the molecular weight of the dextran on the haze intensity is presented in Figure 3. It can be seen that

Table 7.--Inter-laboratory reproducibility of dextran measurements

Sample code #	Dextran, ppm					
	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6
68	955	1385	973	931	990	994
78	1545	1884	1590	1571	1600	1491
89	337	356	244	307	270	370

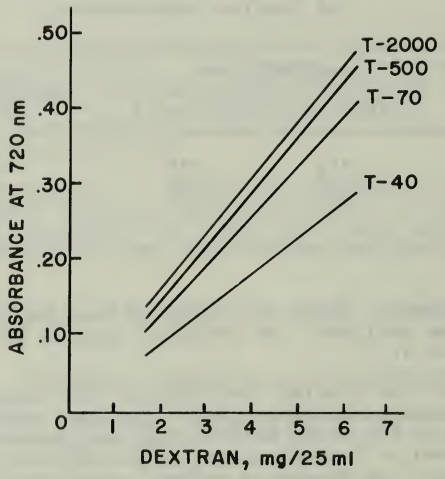


Figure 3.--Standard curves for dextrans of different molecular weights.

the "haze", as measured by absorbence at 720 nm., is not directly proportional to the molecular weight. This should not be surprising because while the scattered intensity (turbidity) is a function of both weight concentration and molecular weight, the absorbance is only related to the weight concentration.

The calibration curve for dextran determinations in this paper was prepared with the commercial dextran T-40 (40,000 M.W.). A lower molecular weight dextran is believed to be more soluble, and more difficult to be removed by refinery processes, and therefore would cause greater problems in sugar refining.

EFFECT OF DEXTRAN CONTENT ON RAW SUGAR POLARIZATION

Upon completion of the examination of the methodology of the Modified Haze Procedure in detail, and setting appropriate standards to be maintained in order to achieve reproducibility, the procedure was used to study the effect of dextran in raw sugar on refinery performance.

Elevation of Raw Sugar Polarization Due to Dextran Content. It is well documented in the literature that dextran is a dextro-rotary compound, having a specific rotation of at least three times that of sucrose ($[\alpha]_D^{20}$ > + 199 versus $[\alpha]_D^{20}$ = + 66.53).

Accordingly, sugars containing an appreciable amount of dextran are subject to a "False Polarization" in the magnitude of three times the Percent dextran concentration or

Elevated Polarization = 3 X % dextran in raw sugar (1)

In order to support this theory, an experiment was designed and conducted, the details of which are as follows:

Four samples of sugar, three raw and one white granulated with varying dextran concentrations were selected. The three raw sugars were washed to remove some color which might interfere with polarization determinations.

Two dialysis membranes, with 12,000 molecular weight cutoffs, were prepared for each sample. Into one was placed a 50 ml. aliquot containing 26 grams of sugar, the other a 25 ml. aliquot containing 13 grams of the same sugar. This sequence was repeated for each of the four samples. These samples were placed in a multiple dialyzer to remove all the sucrose. Time intervals of 2 to 4 days have been reported previously by CSRRP as necessary to remove all the sucrose.

At the end of 95 hours the samples initially containing 26 grams of sugar were removed and filtered through .45u membranes to remove any turbidity that might interfere with polarization readings. The polarizations of the samples were then read with a Rudolf automatic polarimeter. The samples initially containing 13 grams of sugar were removed, filtered and read at

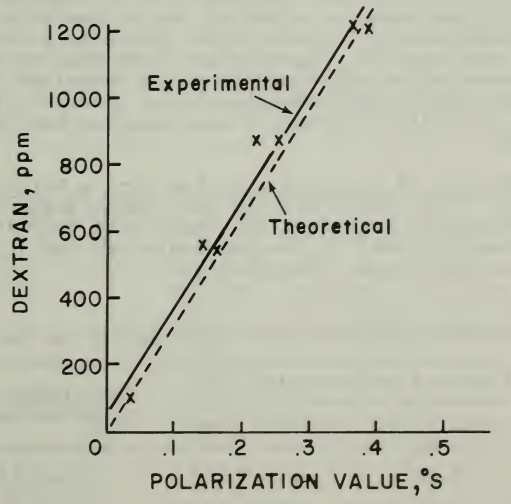


Figure 4.--Polarization values as a function of dextran content.

the end of 163 hours. These four sugar samples were also analyzed for dextran content using the Modified Haze Method.

Linear regression analysis (see graph illustrated in Figure 4) on the data collected yielded a .980 correlation coefficient and the equation of the line is interpreted as follows:

$$\text{Elevated Polarization} = \frac{\text{Dextran in ppm} - 52}{3254} \qquad (2)$$

This equation produces results very close to those calculated from the theoretical equation (1).

Another experiment was performed in order to further verify the above results. A specified amount of T-40 dextran was weighed and transferred into two 100 ml. volumetric flasks, one with water alone and the other with water and 25 grams of sugar.

These samples were polarized along with appropriate blanks and the net increase in polarization recorded. These results appear in table 8 along with calculated results from the theoretical equation (1).

The data collected in these experiments, strongly reaffirms the fact that, dextrans in raw sugar contribute to their net polarizations.

However, since the dialysis study does not eliminate the possible contribution to polarization by compounds (starch and/or protein) other than dextran, an experiment was conducted to resolve this possibility of interference.

Two of the sugars employed in the polarization study were selected. Two sets of solution were prepared from each sugar, and subjected to dextran analysis again. Only this time omitting enzyme and T.C.A. addition in one set, and T.C.A. in the other. To our surprise, the majority of samples exhibited no significant increase in turbidity due to possible starch or protein precipitation. In fact, a net decrease in haze was observed in some samples. Apparently, from the results starch and proteinaceous-like compounds were not contained in the sugars in any significant concentrations. However, the decrease of turbidity observed in some samples has yet to be investigated.

Effect of Addition of Dextranase to Raw Sugars Before Dextran Haze Analysis. The second part of the investigation into the effect of dextran on polarizations deals with checking whether or not the haze produced in the procedure was due in part to any other substance other than dextran.

Table 8.--Dextran polarization: experimental vs theoretical

Dextran g/100 ml	Elevated polarization, °S.		Calculated Polarization, °S.
	with sugar	without sugar	
.1	+1.17	+1.23	+1.10
.3	+3.16	+3.33	+3.31

This was done by treating the four samples of sugar used in the polarization study with dextranase and then analyzing for any residual haze which may have been formed by some other substance using the Modified Haze Procedure.

Experimentally, the enzyme stock solution was prepared according to a paper entitled "Further Studies on Enzymatic Hydrolysis of Dextran in Mill Juices by Dextranase and Fungal Alpha Amylase," by Tilbury and French (1974). Calculations were based on their data as to the minimum necessary dosage required to hydrolyze all the dextran in one hour time at 50°C. This amount was increased by one and one-half times and added to the four samples employed in the polarization study, as well as to a control sample spiked with 800 ppm. of T-40 dextran. The samples were incubated for one hour at 50°C. At the end of this time, the samples were analyzed for dextran as before. The results are listed in Table 9.

The absorbances recorded for the samples after ethanol addition are well below any appreciable or detectable dextran concentration. So it appears that any substance other than dextran, that may have contributed to haze formation, was either hydrolyzed by the dextranase or was in very minute concentrations.

In summary, from the excellent correlation between the experimentally found elevated polarizations and dextran concentrations (.98 correlation), and in turn their strong agreement with the theortically calculated effect of dextran on raw sugar, two statements can be made. These are (1) that the calculated theoretical effect of dextran on raw sugar polarization is supported by these experimental results, and (2) the Modified Haze Method appears to give approximations as to dextran content in raw sugar.

DEXTRAN IN RAW SUGAR AND ITS EFFECT ON SUGAR REFINING

The Modified Dextran Procedure has also been used to analyze the dextran content of raw sugars of different contries of origin. Table 10 gives the distribution of dextran concentration in some raw sugars analyzed. With this information the effect of dextran on refining processes and sugar products was closely monitored at various locations. As a result of this study the threshold raw sugar dextran

Table 9.--Possible interference by other polysaccharides on dextran analysis

Sample	Dextran ppm	Dextran, ppm after dextranase treatment
White gran.	112	nil
White gran dextran added	912	nil
Raw sugar #66	561	nil
Raw sugar #37	872	nil
Raw sugar #87	1221	nil

Table 10.--Dextran content of some raw sugars analyzed

Dextran concentration, ppm	No. of cargos	Cargo in percentage
over 1000	11	10
Between 700-1000	14	13
Between 300-700	33	29
less than 300	54	49

Table 11.--Threshold dextran concentration at which problems manifest

Parameters (Problems)	Dextran in raw sugar ppm (T-40 M Wt)
Raw sugar polarization	300
Raw sugar crystal elongation	600
*Remelt sugar crystal elongation	400
Washed sugar liquor turbidity	350
Cordial product quality	250
Remelt massecuite viscosity (high strike)*	400
*Soft sugar packaging	700
Blackstrap molasses purity	100

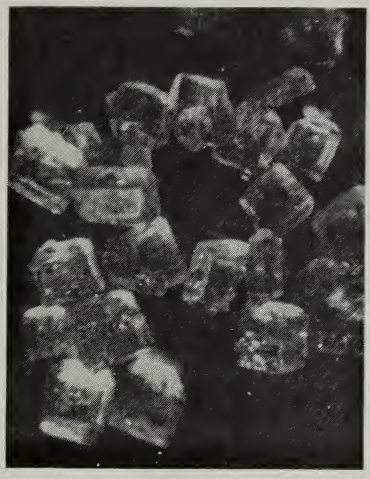
* Data based on a carbonation refinery. The threshold concentrations maybe lower for non-carbonation refinery.

concentrations, at which problems in the processes and products multiplied, were established as shown in Table 11.

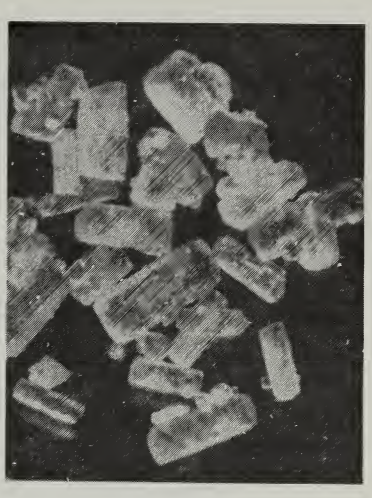
Dextran in sugar products and/or liquors will typically cause increased viscosity, increased turbidity (color), elongated crystals, and elevated polarization, resulting in higher refining costs and additional sugar losses. The dextran-induced problems in each refining unit operation will be discussed briefly in the subsequent section.

EFFECT OF SUGAR REFINING ON DEXTRAN ELIMINATION

A laboratory investigation was undertaken that dealt with the possible removal of dextran through processes generally available to most refineries. These include affination, filtration, clarification, bone char and activated carbon decolorization, and crystallization. All the experimental procedures for the laboratory simulation of the above processes are described in appendix 3. The following section presents the results of this study. The problems attributed to dextran and/or the mechanism by which dextran induces the problems are also discussed.



a. Raw sugar containing <300 ppm dextran.



b. Raw sugar containing ~1500 ppm dextran.

Figure 5.--Effect of dextran on raw sugar crystals.

Table 12.--Separation of dextran by affination process

Sample	Dextran, ppm		% Remained
	Raw sugar	Washed raw sugar	
1	556	486	78.7
2	663	597	81.0
3	550	495	81.0
4	578	550	85.6

Affination. As expected and shown in Figure 5, raw sugar with high dextran usually consists of elongated crystals which will reduce the efficiency of mingling and purging of syrup. To maintain an acceptable washed sugar color, excessive washing will be needed. This will increase both affination syrup purity and volume resulting in higher energy usage.

Table 12 indicates that about 20% by weight of the dextran was carried off with affination syrup. This dextran, together with that contained in low granulated syrup will cause elongation of remelt crystals and introduce smears in massecuite, thereby resulting in increased purity of blackstrap and reduced yields involving repeated boiling. Excessive and occasionally unmanageable high viscosity in remelt high strike massecuite often can be traced to the melting of raw sugar containing more than 400 ppm. dextran.

Table 13.--Dextran content before and after press filtration

Sample	Dextran, ppm		
	Feed	60°C effluent	80°C effluent
1	495	506	501
2	385	380	385

Table 14.--Inability of clarification process for dextran removal

Process	Dextran, ppm	
	Before treatment	After treatment
Carbonatation	860	962
Phosphatation	858	886
Phosphatation with cationic surfactants	1676	1662

Since about 80% of dextran in raw sugar remains in the washed raw sugar, the dextran related problems can be observed throughout the refining process.

Filtration. Table 13 shows the inability of the press filtration to remove dextran. This will result in high nephelos of liquor. Raw sugar with more than 250 ppm. dextran usually will cause difficulty in producing cordial type sugar and in meeting specifications of liquid sugar made from No. 3 and No. 4 sugars even with increased earth usage in the process. Additional washing of white sugar and occasional remelting of No. 3 and No. 4 sugars in order to reduce the final product turbidity (color) will increase energy usage. Soft sugar produced from raw sugar with more than 700 ppm. dextran will experience flowability problems due to stickiness and/or abnormal crystal shape and therefore a reduction in production rate.

The effect of increased viscosity due to dextran will also slow down remelt press filtration. Occasionally, excessive filter aid is needed to maintain a standard melt rate.

Clarification. Both carbonation and phosphatation with or without cationic surfactants did not remove dextran from the liquor treated as shown in Table 14.

High viscosity induced by dextran will affect phosphatation in at least three areas: the rate of flocculation; the flotation rate of coagulum; and the rate of scum compression. A typical curve of flotation velocity as a function of liquor viscosity is depicted in Figure 6.

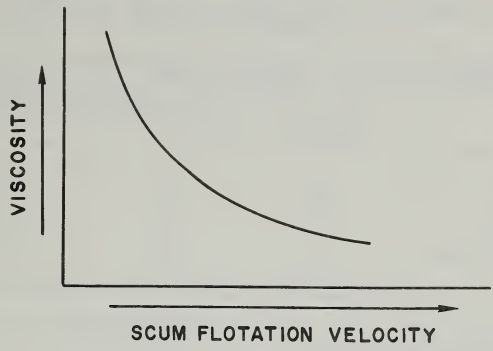


Figure 6.--Floatation rate as a function of liquor viscosity.

Table 15.--Non-adsorption of dextran by carbonaceous adsorbents

Adsorbent	Dextran, ppm	
	Feed	Effluent
Char (3rd displacement)	1200	1215
Granular carbon (3rd displacement)	1200	1200
Powdered carbon (batch test)	1200	1225

Retardation of these rates generally results in cloudy effluent and higher mud volume. Filtration of cloudy effluent is also impeded by excessive viscosity from the dextran remaining in the liquor.

Adsorption Process. Both the laboratory column adsorption and batch decolorization tests indicate, that none of the dextran in the feed liquor was adsorbed by the carbonaceous adsorbents (Table 15).

The effect of dextran-induced viscosity on decolorization by adsorbents can be easily understood in terms of diffusion theory of sugar colorants adsorption (Chou and Hanson 1971). This commonly accepted theory points to the fact that the rate of adsorption is a function of film diffusion coefficient and surface film thickness. The former decreases and the latter increases both with increasing liquor viscosity. It follows that any increases in viscosity will reduce the decolorization. In addition, dextran macro-molecules will also interfere with diffusion of sugar colorants to the adsorbent's surface.

Sugar Boiling. The amount of dextran in liquor occluded into

Table 16.--Occlusion of dextran during crystallization

Sample*	Dextran, ppm		% dextran retained in sugar
	Starting liquor	Crystallized sugar	
WSL	1245	548	17.7
PFWSL	538	375	27.9
#1 Liquor	581	384	26.4

* Raw sugars with widely different dextran content were used.

sugar crystals during the crystallization process is listed in Table 16, using a 40% yield in the laboratory centrifugal. From the results it can be seen, that on the average 24% of starting dextran remains with the finished product, while 76% is channelled back into the refinery streams.

The effect of dextran on sugar boiling can be best illustrated by the rate equation of sugar crystallization (Khamskii 1969).

$$\frac{dM}{dt} = \frac{D}{\delta} .S.C. \qquad (3)$$

Where, dM/dt is the rate of crystal growth in terms of wight increases per unit time, D is the diffusion coefficient, δ the thickness of the diffusion layer, S the effective surface area and C the degree of supersaturation. Dextran-elevated viscosity will decrease the diffusion rate, increase the thickness of the diffusion layer and indirectly reduce the degree of supersaturation, because of the decreased heat transfer due to high viscosity. Dextran-induced elongation of sugar crystals, other things being equal, will reduce the effective surface area for crystal growth.

The overall effect of these difficulties in sugar boiling is reduced yield, increased in-boiling and sucrose loss, and poor product quality resulting in additional refining cost.

CONCLUSIONS

1. The revised "haze procedure" must be adhered to strictly for best reproducibility of test results.

2. The reproducibility of the revised procedure was within ± 3% in intra-laboratory collaborative testing, and ± 10% in inter-laboratory study.

3. Dextran-elevated raw sugar polarization was found to be mathematically proportional (corr. coeff. 0.98) to the dextran concentration, based on a 40,000 molecular weight dextran standard.

4. In most cases, the threshold dextran concentration in raw sugar, at which additional expenses would be incurred by the sugar refiner, was determined to be 300 ppm.

5. Most processes available to the sugar refiner were found to be ineffective in dextran removal.

6. Dextran-induced problems in sugar processing can be explained in terms of the physical chemistry of the sugar solutions containing dextran.

APPENDIX 1

Relationship Between Cell Length and Absorbance

Experimentally, a number of pure T-40 M.W. dextran solutions were prepared, and analyzed with varying cell lengths. These absorbance values were then converted mathematically (assuming a Beer's law relationship) to absorbance per one cm. cell length. This was done to provide a uniform means of comparison. Refer to Table 1A for detailed results.

TABLE 1A

Concentration of Dextran Soln. T-40, mg/25 ml.	Cell Length Cm.	Absorbance at 720 nm. Per 1 Cm.
.6	5	.013
	10	.013
1.0	5	.029
	10	.029
2.0	2	.079
	5	.081
3.0	2	.144
	1	.132
4.0	1	.201
	2	.205

The results show that the difference between readings for the same dextran solution measured with different path lengths fell within $\pm$ 5% difference.

The Effect of the Order of Addition of Water and Ethanol On Haze Formation

An experiment which dealt with the effect of the order of addition (water and ethanol) on the haze formed for a given concentration of dextran was conducted. Experimentally, five standard dextran solutions of the same concentration (5 mg/25 ml) were prepared according to ICUMSA procedure. The samples were coded A through E for identification purposes. Sample A was precipitated by the addition of 200 proof anhydrous ethanol, and served as the control. Sample B was precipitated with 190 proof, sample C with a laboratory prepared 190 proof ethanol made by the dilution of 200 proof anhydrous grade with water. Sample D and E were precipitated in a similar manner as sample C. The anhydrous 200 proof ethanol was used as the precipitating agent for both sample D and E. However, a proportional amount of water was added before ethanol in sample D, and after ethanol in sample E, to produce approximately the same effect as precipitation with 190 proof ethanol.

The results of the experiment, refer to Table 1B, reaffirms previous findings in regard to haze intensities formed by 190 versus 200 proof ethanol as described in "The Effect of the Alcohol vs Water Ratio on Haze Formation" in the text.

TABLE 1B

Sample Code	Absorbance (at 720 nm)
A	.508
B	.290
C	.295
D	.288
E	.290

The results also show, that the concentration of ethanol and/or water at the point of addition, and the order in which they are added, have no effects on the intensity of the haze formed. This can be seen by the insignificant differences in the absorbances measured for samples B, C, D and E.

The Effect of Varying the Final Sugar Solids Content on Dextran Haze Formation

The ICUMSA procedure and calculations are all based on the premise of a initial sample size of 23.5 grams of raw sugar or 50 mls. of 40 Bx. solution, and total recovery of the sample throughout the analysis.

This experiment was designed to measure the effect of varying the above concentration, so that the sugar content in the reaction flask was greater or less than the expected final concentration of 2.67 grams in the 25 ml. of test solution.

The details of this experiment were as folows: a sample of raw sugar was prepared in duplicate and both samples analyzed for dextran using the Modified Haze Method up to the collection of the final filtrate. These samples were initially prepared to be on the high side of the desired final filtrate concentration. Four aliquots of varying volumes were taken and transferred to 25 ml. volumetric flasks. The samples were diluted as necessary, in order to vary the solids content and still maintain the same total aqueous volume of 12.5 ml. in the flasks. The solids concentration in the four flasks were 3.52 g, 3.15 g, 2.77 g, and 2.27 g, respectively.

The samples were then precipitated by the addition of 200 proof anhydrous ethanol. The quantity of dextran contained were determined by referral to the standard calibration curve. Next the ppm dextran for each sample was calculated in two different manners, (1) assuming a ideal concentration of 2.67 g, and (2) correcting for the real concentration of solids contained in the samples. The results are listed in Table 1C.

From the results, it can be seen immediately that varying the solids content affects proportionally the amount of absorbance measured and in turn the mgs. of dextran determined. It follows that if the solids content in the reaction flask deviates significantly from the desired 2.67 g concentration, erroneous results will be obtained unless the ppm dextran value is calculated on the basis of the actual final concentration.

TABLE 1C

Sugar Concn. g/25 ml.	Absorbance Measured	mg of Dextran Determined	ppm Dextran Based On Std. 2.67 g/25 ml.	ppm Dextran Based On Actual final Concn.
3.51	.314	3.34	1251	952
3.15	.274	3.00	1124	952
2.78	.234	2.65	993	953
2.27	.186	2.25	854	991

However, it is our experience based on numerous tests using this procedure, that the solids content usually remains in the range of 2.62 to 2.73 g. Assuming 2.67 grams/25 ml. for the calculation of ppm dextran would only result in differences in the magnitude of 2 to 3%. In certain cases where the filterability of raw sugar is extremely poor, the actual final concentration will deviate significantly from the standard 2.67 g/25 ml. due to evaporation during the prolonged filtration.

APPENDIX 2

The Effect of pH on Dextran Haze Measurements for Raw Sugar

Interest in the effect of pH on dextran measurements was initiated as a result of findings obtained in other non-related experiments. Specifically, upon investigating the effect of clarification processes on dextran removal, a contradiction in results was obtained. Namely, the dextran content of the clarified liquor was higher than that of the feed liquor to the clarifier.

The first experiment was designed to isolate the cause of this inconsistency. A sample of washed sugar liquor was prepared and split into four equal portions. Three of the samples were treated with .2% CaO on the solids basis.

The pH of two of these samples was adjusted by the addition of dilute HCl to 6.8 and 5.0 respectively, before the addition of the enzyme. The fourth sample was maintained as a control. The results of the dextran analysis on these samples is listed in Table 2A.

TABLE 2A

Sample	Initial pH	pH Adjusted Before Enzyme Digestion	Dextran ppm
Control	6.0	6.0	110
.2% CaO added	10.2	5.0	125
.2% CaO added	10.2	6.8	120
.2% CaO added	10.2	10.2	250

From the results it can be seen that adjusting the pH, within the range of 5.0 to 7.0 pH, has for the most part compensated for the effect of the addition of the CaO. One explanation would be that the enzyme added for starch hydrolysis was deactivated at elevated pH.

Another experiment was conducted to verify this theory. A sample of sugar liquor was prepared and divided into three

equal portions. Two of the samples were adjusted to 10.2 pH, one by the addition of CaO, the other by NaOH, after the enzyme addition and digestion period. The third sample served as the control. The results of dextran analysis on these samples are listed in Table 2B.

TABLE 2B

Sample	Initial pH	pH Adjusted After Enzyme Digestions	Dextran pppm
Control	5.9	5.9 (No adjustment)	121
1	5.9	10.2 (adjusted with CaO)	148
2	5.9	10.2 (adjusted with NaoH)	132

The results indicate that a high pH after enzyme digestion has no appreciable effect on dextran analysis. This finding tends to support the theory that the increase in pH reduce the effectiveness of the enzyme causing an increase in the intensity of haze formed, which is not truly representative of the real dextran content.

A final experiment was run in order to clearly rule out the possibility that the calcium oxide was a major causative factor in producing the increased haze values. The results of this experiment and the conclusions drawn from the cumulative study are discussed under "Effect of pH on Dextran Haze Measurement" in the text.

APPENDIX 3

In subsequent sections listed below, are the detailed experimental procedures used for laboratory simulation of the refinery processes discussed under "Effect of Sugar Refining on Dextran Elimination" in the text.

Affination

A laboratory-scale raw sugar affination process was designed, the details of which are as follows:

1000 grams of well mixed sample were placed in a mixer at low speed. 380 mls. of 64° Brix granulated sugar syrup at room temperature were added slowly from a dispensing burette at a uniform rate for 5 minutes. The sugar and syrup were then mixed for an additional one minute making the total mingling time 6 minutes.

The resulting magma was transferred into a centrifugal machine which was brought to 3000 RPM in approximately 15 seconds. The sample was spun for exactly two minutes and then air dried for approximately one hour.

Press Filtration

To simulate refinery press filtration a standard bomb filtration apparatus, whose design was adapted from a unit developed by John's Manville Research Laboratory, was employed. The details of the test are as follows:

Samples of washed raw sugar to be filtered were selected and 60° brix sugar liquor prepared from them. John's Manville

Standard Supercell at 0.35% on sugar solid was added to each sample (admix). The liquors were then filtered, first under the conditions of 60°C and 50 PSI, and then again at the elevated temperature of 80°C. and 50 PSI. Representative samples of the feed and effluent liquors were collected for later analysis.

Clarification Processes

Carbonation: A laboratory batch-scale carbonation process was designed, the details of which are as follows: Approximately 500 grams of washed sugar liquor was transferred to an appropriate container. To this liquor was added between .7 to .76% CaO on a solid basis. The liquor was then heated to approximately 80°C, at which point CO_2 gas was introduced into the liquaor until the pH was about 8.2. The liquor (with one gram of earth admix) was then filtered by means of a vacuum filter assembly, fitted with Reeves Angel #202 filter paper precoated with #2 standard earth.

Samples of the treated and untreated liquors were collected and saved for later analysis.

Phosphatation: A laboratory scale phosphatation process was conducted on samples of washed sugar liquor. The details of the procedure are as follows:

500 grams of washed sugar liquor were heated to approximately 75°C. at which point .025% P_2O_5 was added in the form of phosphoric acid solution. The pH was then adjusted to approx. 7.2 by the addition of calcium saccharate solution. Next 8 ppm on a sugar solids basis of polyacrylamide was added to assist in scum flotation. The sample was then transferred into 100 ml Nessler tubes with bottom outlets. These tubes were placed into a water bath thermostated at 90°C for approximately 30 minutes, or until all scums had floated to the top. The clear bottom liquor layer was then drained off and filtered through Reeves Angle # 202 filter paper to remove any suspended impurities.

Phosphatation plus Cationic Surfactant Additives: As in the previously described phosphatation procedure, the steps followed were similar except for the addition of 350 ppm of a cationic surfactant before the polyacrylamide addition.

Adsorption Processes

Bone Char and Granular Carbon: This experiment entailed the simulation of refinery decolorization column filtration. Bench scale laboratory columns were prepared and filled with the appropriate adsorbent granular carbon or bone char. The columns were jacketed to maintain a feed temperature of approximately 80°C. The flow rate was controlled by means of a Technicon Auto Analyzer pump and appropriate tubing to a nominal value of 1.2 ml/min.

The feed liquor, approximately 60°Brix concentration, was prepared from a washed raw sugar. The effluents were collected in fraction approximately 24 mls in volume every 20 minutes.

Two sample composites, one made from the combination of fractions 7-12, and the other from fractions 47-52 (equivalent

to approximately the 3rd and 17th weight displacements) were prepared and used for later analysis.

Powdered Activated Carbon: This experiment was designed to simulate the use of powdered activated carbons in the refinery.

The details of the experiment are as follows: A sample of 60°Brix washed sugar liquor was prepared. The pH of the liquor was adjusted to 7.0 ± .05. The sample was then split into five equal portions each containing 250 grams of liquor. The samples were then transferred to a water bath and heated to 80°C. At this point four samples were treated with about .3% of activated carbons of various suppliers. The fifth sample was retained as a control. The total contact time for the carbon and liquor was held to 20 minutes. At the end of this time, the liquors were vacuum filtered to remove suspended carbon.

Crystallization

A laboratory unit was set up to simulate, as closely as possible, the operating conditions of a refinery vacuum pan. The apparatus adopted for this purpose consisted of a rotary flask used as a vacuum pan, a constant temperature water bath at 155°F as heating media for evaporation, and a refrigerated water bath at 40°F used for condensation of vapor from the flask.

The details of the procedure are as follows: 1000 grams of process liquor to be crystallized were transferred to the rotary evaporator flask. The liquor was concentrated to 76.5°Brix at 29" vacuum. At this point the liquor was seeded with one gram of finely ground sugar seed crystals and continued to "boil" at a vacuum of 24" for one additional hour. The resulting magma was transferred to a centrifuge and spun at 3000 rpm for 15 minutes. The sugar was air dried and stored for subsequent analysis.

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DISCUSSION

E. ARIAS (Sugar Cane Growers Coop. of Fla.): Would you elaborate the reasons for using forty thousand molecular weight dextran as standard?

C. C. CHOU: There are at least three reasons for the use of T-40: 1. Our dialysis study indicates that there is an excellent correlation between the elevated polarization and the dextran concentration using a 40,000 molecular weight dextran standard. 2. Small molecular weight dextran is more soluble in water and difficult to remove, and therefore has greater detrimental effect in the sugar refining processes. In fact, 2 million molecular weight dextran is only soluble in boiling water. There is another school of thought which postulates that higher molecular weight dextran has greater effect than lower molecular weight dextran. This may not be the case if we analyze the characteristics of the dextran - induced problems: (a) Elevated polarization - both high and low molecular weight dextran will elevate the polarization. We are very conservative in using 199 as the specific rotation of dextran. (b) Elongated Crystals - It has been shown that the elongation of crystals is primarily related to the structure of dextran, particularly to the degree of α (1-6) lingages. (c) Increased Viscosity - Viscosity measurement cannot distinguish between particles of different size but same shape and degree of hydration. Viscosity is very sensitive to the molecular shape and degree of hydration. Therefore, unless the shape and the degree of hydration vary with molecular wt., which may or may not be the case, the viscosity is not directly proportional to the molecular wt. (d) Increased turbidity (color) - High molecular weight dextran will give higher turbidity which is a function of both molecular weight and weight concentration. However, color is only related to the weight concentration. 3. Dextran is a polymerization product of sucrose initiated/formed by Leuconostoc organism. Under this heterogeneous environment, the reaction kinetics is not likely to favor production of exceedingly high molecular weight dextran in very large quantity .

A. RAPPOLD (Godchaux-Henderson): Is the modified ICUMSA haze method specific enough for general use in the cane sugar manufacturing industry?

C. C. CHOU: The specificity of the haze procedure for dextran analysis may or may not satisfy the high demand of those scientists who wish to study pure compounds. However, in the manufacturing industries, quite often the best available and the most practical technology/technique have to be used for particular process and quality control purposes. A typical example in the sugar industry is the measurement of color. In this measurement, the types and structures of sugar colorants are not specifically identified. Instead, the "color" levels of sugar and sugar related products are established to monitor and to assess the extent at which these sugars and sugar related products will affect the refining performance and product quality. Based on the same philosphies and to serve the same primary purpose, I believe that the haze procedure is specific enough for the cane sugar manufacturing industry as illustrated in our work presented today by others' work published elsewhere.

J. POLACK (Audubon Sugar Inst.): Is dextranase treatment of the raw sugar sample part of your routine haze test procedure?

C. C. CHOU: Dextranase treatment was done on selected random raw sugar samples only. For those samples treated with dextranase, the haze developed in 50% ethanol solution was insignificant.

M. A. CLARKE: What molecular weight dextran was used as a standard for measurement in your section on the effect of refinery processes on dextran removal?

C. C. CHOU: Dextran of forty thousand molecular weight was used as standard for measurement throughout our study.

M. A. CLARKE: Your study appears to support our theory that low molecular weight dextrans are the major problem dextrans in the sugar refinery.

F. G. CARPENTER (Southern Regional Lab.): The elongation of the sugar crystals does not necessarily reduce the geometric surface area. Also the percent alcohol used for haze development should be high enough to ensure precipitation of all dextran.

C. C. CHOU: Your last comment is well taken. Alcohol concentration higher than 50% probably would be needed for complete precipitation of dextran.

M. A. CLARKE: With regard to the concentration of alcohol used for dextran precipitation: a great deal of work has been done on this point in Australia, South Africa and elsewhere. (F. K. R. Imrie and R. H. Tilbury 1972. Polysaccharides in sugarcane and its products. Sugar Technology Reviews 1: 291-361. — J. S. Keniry, J. B. Lee and V. C. Mahoney 1969.

Improvements in the dextran assay of cane sugar materials. Int. Sugar Jour. 71: 230-233. -- R. P. Jennings 1964. Proc. Ann. Congr. S. African Sugar Technol Assoc. 38: 8792.) The general conclusion is that an alcohol content of 50% will precipitate over 90% of dextrans; an alcohol content above 50% will precipitate other high molecular weight compounds (other "gum" components) in addition to dextran and will confuse the analysis.

C. C. CHOU: The geometric surface area per unit weight of sugar may or may not decrease due to elongation depending on the number of crystals per unit weight. However, the effective surface area for crystal growth should decrease due to crystal elongation, other things being equal.

M. C. BENNETT (Tate and Lyle): In view of the fact that dextran probably adsorbs only on specific faces of the sugar crystal, both Drs. Carpenter and Chou's comments are valid in the specific condition mentioned.

Would you clarify your findings that while about 80% of dextran remained in sugar crystal after affination, there was about 20% of dextran occuluded in sugar crystal during sugar boiling?

C. C. CHOU: Our data indicate that about 20% of dextran in the feed liquor was occluded into the sugar crystals during crystallization. When these sugar crystals were processed through the affination step, 80% of that 20% "occluded" dextran remained with the affined crystals.

ISOLATION AND IDENTIFICATION OF CONSTITUENTS CONTRIBUTING TO ODOR AND FLAVOR IN SYRUPS AND BROWN SUGARS

Mary An Godshall and Earl J. Roberts

Cane Sugar Refining Research Project, Inc.

INTRODUCTION

Brown sugars and syrups are sold primarily because of their desirable flavors, but little objective information is available about factors that contribute to the flavor of these products. What flavor control exists is usually intuitive or even accidental, a fortunate byproduct of the refining process. Most of the time, this lack of information may seem to be irrelevant since, year after year, tons of these products are successfully produced and sold, and the conclusion might be made that the process is performing adequately. However, when off-flavors affect customers' products and the customer complains, or when competing products begin to make inroads into sales, or when traditional methods of processing are changed to newer methods, the matter of flavors, odors, and tastes may become very important.

Brown sugar is sold on the basis of color, moisture, and crystal size. No mention is made in any specifications as to flavor or odor. In the Cane Sugar Handbook, flavor is not mentioned in connection with brown sugar. To our knowledge, only one paper has been published regarding brown sugar flavor (Christianson and Anheiser 1980).

Several approaches are available in attempting flavor control of a product. The first is the subjective approach which depends either on expert taste panel results or on one individual who is empowered by virture of his expertise to make decisions about a product's acceptability. When this mechanism for quality control does not exist in a company, the need to control or manipulate flavor is often activated on the basis of customer complaints about the product. This is the situation that usually exists in the sugar industry.

A second, objective approach to flavor analaysis and control is, in its purest form, undertaken in a research laboratory. It involves the isolation, identification and measurement of individual constituents, and its ultimate goal is to recreate the original flavor of a product from its individual components. In reality, this is seldom possible except with simple foods containing a few major flavor ingredients. The development of artificial fruit flavors is one successful example of this approach.

A third approach combines the subjective and objective approaches. Here, the goal is to identify the constituents that contribute most to the flavor impact and to focus on these compounds.

Industries such as tobacco, tea, coffee, and wine have traditionally had strong programs for sensory evaluation of their products coupled with identification of constituents responsible for flavors and odors. They often modify or enhance their products by addition of natural and artificial flavors.

Cane Sugar Research has had extensive experience in isolating and identifying minor consituents in sugar (Farber and Carpenter 1971, 1975). In most cases, the emphasis of this work has been on the relationship of minor constituents to color formation. Recently, some of the emphasis has switched to identification of compounds that contribute to odor and flavor (Godshall et al. 1979, 1980). Not surprisingly, the two types of research overlap, and information gained for one objective, that is, the elucidation of color formation, often gives useful insight and direction to the flavor phase of this research. Colorant precursors are often small molecules that contribute flavor to sugar products.

Sensory evaluation involves the interaction of several disciplines--psychology, mathematics, and chemistry among others. A complete flavor profile involves identification and subsequent quantification of compounds responsible for odor or flavor, determination of interactions such as masking or synergism of flavors at subthreshold levels, and sensory evaluations by trained panels.

This report will summarize preliminary work leading to flavor profiles of brown sugar.

EXPERIMENTAL

Sources of Samples

Materials used for analysis consisted of six commercial brands of light brown sugar. All sugar were processed with bone

char. Two batches of sugars A and E, processed about 12 months apart, were analyzed. Freshly regenerated and exhausted bone char from the manufacture of sugars B, E-1 and E-2, new char from the manufacture of sugar E-1, a sample of sweetwater off char, and one of equipment rinse water used in the manufacture of sugar B were analyzed. Sugar E was a coated sugar, and its coating syrup was analyzed. The other sugars were crystallized from process syrups.

The samples analyzed are listed in Table 1. Letter codes refer to refinery of orgin, not to grade of sugar.

Source of Standards

Authentic compounds were obtained from various chemical supply houses and purified by recrystallization if not chromatographically pure.

Table 1.--Samples analyzed

Sugar	Other products analyzed from same refinery
A-1	---
A-2	---
B	Regenerated char
	Exhausted char
	Sweet water off char
	Equipment wash water
C	---
D	---
E-1	New char
E-2	Regenerated char
	Exhausted char
	Coating syrup
F	---

Acetyl formoin (3,5-dihydroxy-2,5-dimethyl-2(H)-furanone) was synthesized by the method of Goto et al. (1963).

Furaneol (3-hydroxy-2,5-dimethyl-2(H)-furanone) was synthesized by boiling rhamnose with piperideine acetate in ethanol, as suggested by Hodge et al. (1963).

Isomaltol (3-hydroxy-2-acetylfuran) was synthesized by the method of Hodge and Nelson (1961).

Analysis of Volatiles

Volatile profiles were obtained on a Model 5750 Hewlett Packard Gas Chromatograph modified with an external injection chamber (Legendre et al. 1979). 300 to 1000 mg of sugar or 200 to 300 mg of syrup was placed inside the sample holder, held in place with glass wool, sealed inside the chamber, and heated to 135°C. The volatiles were swept from the heated sample through a sodium sulfate trap to remove water and volatile fatty acids (VFA) with a stream of helium for 16 minutes and deposited at the head of a 6 ft nickel column packed with Tenax-GC, 80/100 mesh, coated with approximately 7% poly-MPE. The volatiles were separated by programming the column from 50°C to 200°C at 4°C/minute.

Analysis of Acetic Acid as its Phenacyl Ester

Acetic acid was extracted from a 25% solution containing 35 g of sugar with pH adjusted to 2.2 with 2N sulfuric acid. Extraction was performed in a continuous liquid-liquid extractor for 5 hours with ether. One ml of triethylamine (TEA) was added to the ether in the solvent flask to complex the acids as they were extracted.

Extracts were dried from 2 hours to overnight with calcium sulfate, filtered, and evaporated to dryness without heat in a rotary evaporator. The sample was reacted with 2 ml phenacyl bromide in acetone (approximately 30 mg/ml or enough to provide a molar excess) and 0.1 ml TEA in acetone (about 14 mg/ml). An appropriate quantity of triphenylmethane (TPM) in acetone was added as the internal standard for quanitation. Derivatization of the acid to the phenacyl ester took 4 hours at room temperature. This time could be shortened by heating the reaction mixture at 40°C for 2 hours. Derivatives were stable for two days.

Glacial acetic acid was reacted in the same manner to determine its relative response value to the internal standard, TPM.

The acids were anlayzed by conventional GLC on a 7 ft nickel column packed with 6% OV-101 on Chromosorb Q, 100/120 mesh. Separation took place by programming the column for a 4 min hold of 100°C, then increasing the temperature 6°C/min to 250°C. The injection port temperature was 280°C, and the flame ionization detector temperature was 300°C.

Extraction of Less Volatile Compounds

One hundred grams of sugar or an equivalent amount of syrup was acidified to pH 2.2 with 2N sulfuric acid and extracted with redistilled ether in a separatory funnel.

The ether extract of an acidified solution of sugar A-1 was further fractionated into an acidic and a phenolic fraction by swirling the ether extract with 3% sodium bicarbonate to remove acids. The remaining ether solution contained the phenols and was treated in the usual manner. The sodium bicarbonate solution was acidified with sulfuric acid and the acids re-extracted with ether and the extract prepared in the usual manner.

Five hundred grams of bone char was poured into an 8 cm diameter glass column with a perforated porcelain plate in the bottom covered with glass wool. Spent char was first soaked overnight in methanol to remove residual sugar. The methanol was concentrated to a small volume for thin layer chromatography (TLC) and gas liquid chromatography (GLC). One liter of ether was poured over the char in the column and slowly drained off over a period of 2 to 3 hours. The preliminary methanol washing was omitted for the new char and freshly regenerated char.

Extracts were dried with sodium sulfate and filtered. It was not necessary to dry the bone char extracts. The extracts were concentrated to a small volume for analysis by TLC; solvent was completely removed for analysis by GLC.

TLC Analysis of Extracts

Extracts were spotted onto 20 cm x 20 cm silica gel G commercially coated plates. Developing solvent was the upper phase of toluene/ethanol/water/acetic acid (100:28.5:7.5:0.5).

Fluorescence of spots was noted under long wave ultraviolet light. Spots were visualized with the following sprays: (1) aqueous ferric chloride, (2) 2N sulfuric acid and heated 10 min at 100°C, (3) ethanolic anisaldehyde and heated 10 min at 100°C. The latter spray was freshly prepared daily by mixing 36 ml ethanol, 2 ml anisaldehyde, and 2 ml concentrated sulfuric acid.

Spots of particular interest were scraped off the plate and the silica poured into miniature columns made from disposable pasteur pipets. The separated constituents were eluted from the silica with methanol into 3 ml vials, the solvent evaporated off with a stream of nitrogen, and prepared for GLC.

Gas Chromatography

Extracts were redissolved in a minimum volume of pyridine and converted to their trimethylsilyl (TMS) derivatives with hexamethyldisilazane and trimethylchlorosilane in a 2:1 v/v ratio.

The same column and program described for phenacyl bromide derivatives was used for TMS derivatives.

Identification of Compounds

Compounds were identified by comparison of GLC retention times and peak enhancement with authentic compounds, TLC mobility, color rections and combined gas chromatography/mass spectroscopy (GC/MS).

Mass spectra were obtained on a Finnigan 4000 GC/MS with INCOS Data System. Operating parameters were 70eV ionizing potential and scan range from 33 to 650 atomic mass units. The GC/MS system was able to accomodate both conventional injection and external volatiles sampling. Columns similar to those described in earlier sections were used.

RESULTS AND DISCUSSIONS

Volatile Profile

Figures 1 and 2 show the profile of volatile compounds obtained from approximately 1 g each of sugars A-1 and B. Table 2 lists the identified peaks. Identical peaks are given the same number in each sugar to aid comparison. In addition to the compounds listed, ethanol, methanol, and acetaldehyde were identified in both sugars.

It is to be noted that although the majority of volatiles in sugar B were also in sugar A-1, there were significant differences. The absence of 2,3-pentanedione, 2-methyl-3(H)-furanone, and furfural from the profile of sugar B could have considerable impact on its flavor qualities since these are highly flavorful compounds with low taste thresholds, which are especially associated with the caramel flavor.

Low purity sweetwaters used in the production of sugar B were analyzed for volatiles with the external inlet. The char water, which possessed a strong char-like odor contained diacetyl as the major volatile. Diacetyl has a buttery-sweet odor, not a char odor; this would indicate that the compound or compounds responsible for char odor are not extremely volatile. Ethanol, pentane, and acetaldehyde were also identified in this sample. In the equipment wash water, the major volatiles were acetic acid and ethanol.

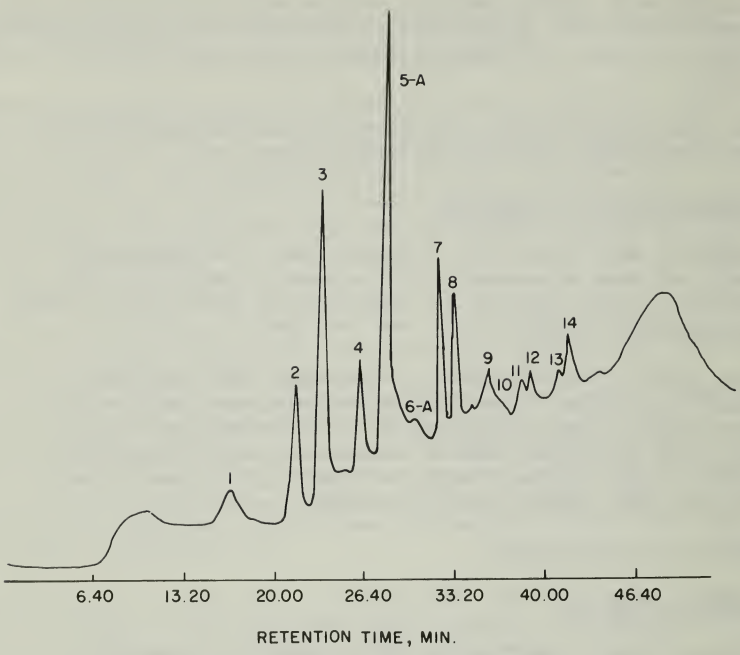

Figure 1.--Volatiles in sugar A-1. Peak identities are listed in Table 2.

Acetic acid

Acetic acid was found to be the most abundant volatile constituent in all light brown sugars analyzed. It was removed from the profile during GLC analysis by passing the vapors through a sodium sulfate trap. If the trap was omitted from the analysis acetic acid was the only compound seen. This is illustrated in Figure 3, in which 0.5 g sugar B was analyzed for volatiles; the acetic acid is so concentrated that the other volatiles were lost in the baseline.

Acetic acid proved to be difficult to quantitate by the direct GC method for several reasons. There was interference from other volatiles, but this was minimal since there was a large excess of acetic acid. The most difficult problem with this analysis was that the extremely polar acetic acid molecule bound to a lesser or greater extent to every

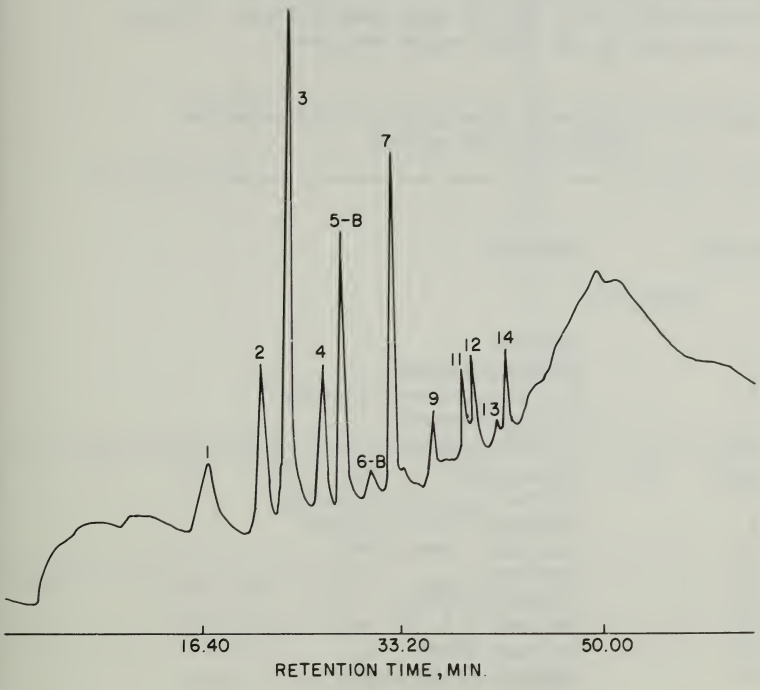

Figure 2.--Volatiles in sugar B. Peak identities are listed in Table 2.

chromatographic support examined. The degree of binding increased as the column aged. The Tenax-GC column gave the best performance of all the columns tested, but an attempt to construct a calibration curve using external standarization was not successful because of poor reproducibility of results.

It was felt that the importance of acetic acid to the volatile profile justified finding a method to measure it. For this reason, a method based on the reactivity of phenacyl bromide to acids was developed.

Table 3 lists the results of acetic acid determination of several samples. The results indicate that low purity rinse water is the source of acetic acid in Sugar B. The coated sugar (E) had an amount of acetic acid similar to the other sugars. Sugar F was very high; this sugar was manufactured by a process that utilized a high percent of molasses.

Phenacyl bromide will react with other volatile fatty acids as well, so it could be determined if other volatile acids were present. Figure 4 shows the phenacyl esters of sugar E-2, a coated sugar. Formic and butyric acids were present in a concentration of 57 and 11 ppm, respectively. Formic acid was not seen in any other sugar analyzed.

Table 2.--Compounds identified in the volatile profile of two sugars

Peak No.	Compound
	Sugar A-1
1	Pentane
2	2-Methylpropanal
3	2,3-Butanedione (diacetyl)
4	3-Methylbutanal
5A	2,3-Pentanedione
6A	1-Pentanol
7	Hexanal
8	2-Methyl-3(H)-furanone
9	Heptanal (tentative)
10	Furfural
11	2-Pentyl furan
12	Unknown (43, 41, 44, 56, 57, 84)*
13	3-Hexene-1-ol
14	Nonanal (tentative)
	Sugar B
1	Pentane
2	2-Methylpropanal
3	2,3-Butanedione (diacetyl)
4	3-Methylbutanal
5-B	Pentanal
6-B	3-Methyl-1-butanol
7	Hexanal
9	Heptanal (tentative)
11	2-Pentyl furan
12	Unknown (44, 41, 45, 57, 43, 84)*
13	3-Hexene-1-ol
14	Nonanal (tentative)

*Numbers in parentheses refer to major ions in the mass spectral fragmentation pattern.

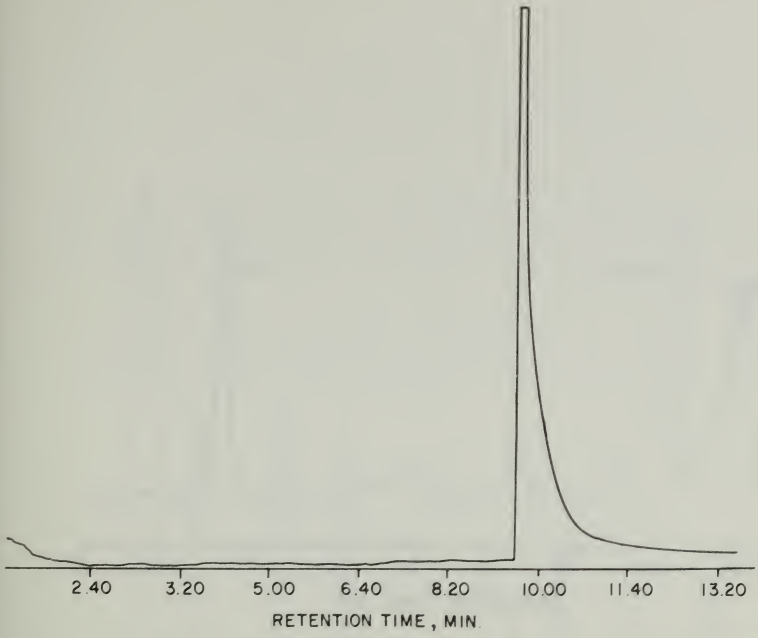

Figure 3.--Acetic acid in 0.5 g sugar B.

Table 3.--Acetic acid in samples

Sample	HAc, ppm
Sugar B	72, 87
Sweetwater off char, B	none detected
Equip. rinse water, B	126
Sugar C	132
Sugar D	184
Sugar E-2	133
Sugar F	372

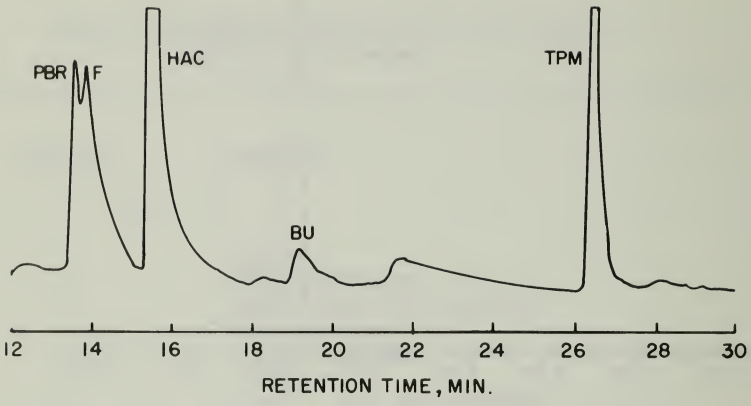

Figure 4.--Phenacyl bromide esters in sugar E-2. PBR = phenacyl bromide; F = formic acid; HAc = acetic acid; BU = butyric acid; TPM = triphenylmethane (internal standard).

Acetic acid has a flavor threshold of 54 ppm in water (Teranishi et al. 1971). An informal taste panel consisting of 8 trained tasters and 4 untrained tasters determined the threshold of acetic acid to be 100 ppm in 50% sugar solution; the odor threshold was 50 ppm. The panelists, however, did not preceive the flavored solutions to be similar to brown sugar flavor and all felt the flavor was mild but unpleasant. Since acetic acid occurs in light brown sugars at or above its flavor threshold, the implication is that some other compound or compounds are interacting with it to mask the majority of the unpleasant acetic flavor. However, it is still possible to detect the tingling acid sensation of acetic acid in brown sugar and to detect its odor, which several panelists were able to do once they became familiar with this attribute.

GLC and TLC of Extracts

The chromatogram of the TMS derivatives of the acidic fraction of the ether extract of sugar A-1 is shown in Figure 5; the peak identities are listed in Table 4.

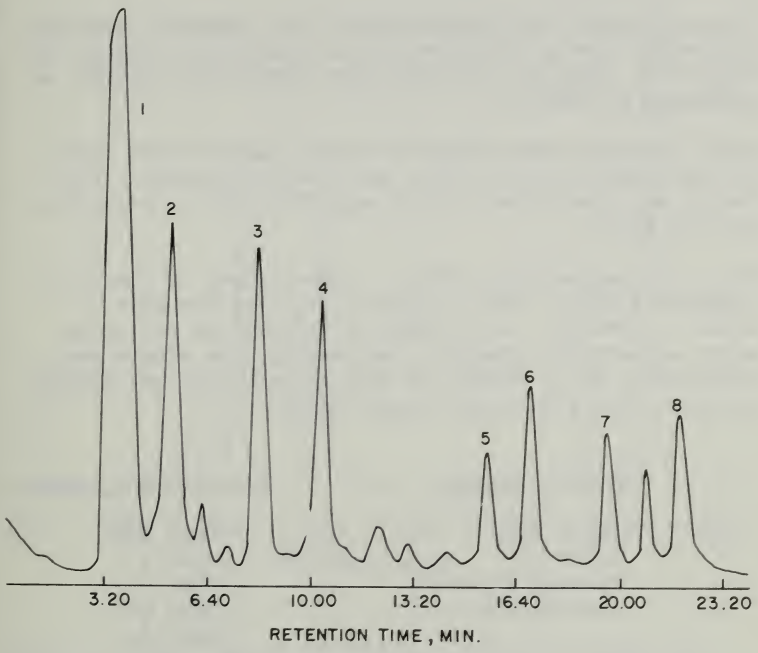

Figure 5.--Acidic fraction of ether extract of sugar A-1. Peak identities are listed in Table 4.

Table 4.--Compounds identified in the acid fraction of an ether extract of sugar A-1

Peak No.	Compound
1	Lactic acid
2	2-Hydroxybutyric acid
3	Benzoic acid
4	Methyl succinic acid
5	2-Hydroxybenzoic acid (salicylic acid)
6	4-Hydroxybenzoic acid
7	Vanillic acid
8	3,4-Dihydroxybenzoic acid
9	Syringic acid

The phenolic fraction of the same ether extract of sugar A-1 showed the presence of diethylene glycol, catechol, and resorcinol. Catechol was the major peak in the phenolic extract as well as the major spot visualized with ferric chloride on TLC.

Figure 6 shows the chromatogram of the compounds extracted with ether from a saturated sodium bicarbonate solution of sugar A-1. Five of the peaks were identified by GC/MS, as indicated in Table 5.

Other compounds identified in various samples were maltol, hydroxymethylfurfural (HMF), and 4-methylcatechol. The latter was identified only in sugar E-1 and its respective coating syrup.

Phenolic compounds contribute a wide variety of flavors to foodstuffs (Maga 1978), ranging from spicy-aromatic to smokey. However, the presence of catechol as one of the major extractable phenolic compounds in some sugars was unexpected, and a survey was made to see if it was always present. The results are listed below:

Catechol present	Catechol not present
Sugar A-1	Sugar A-2
Sugar E-1	Sugar B
Coating syrup E-1	Sugar C
Coating syrup E-2	Sugar E-2
	Sugar F

The results indicated that catechol was not present in most sugars. It probably entered the sugar when the char was nearing exhaustion or the level going on to char was too high to remove. We found that catechol forms an ether-insoluble complex with iron, and the presence of iron may serve to eliminate it from the extract. The results for the sugars from the same refinery (pairs from A and E) show that a great deal of variation can exist with any one process.

There are two possible sources of catechol, the sugarcane plant and carbohydrate degradation. Catechol is a metabolic breakdown product and may have carried through the process from the sugarcane plant. A number of polyhydroxy phenols, including catechol, were reported by Popoff and Theander (1972, 1976) to be carbohydrate degradation products under a variety of conditions.

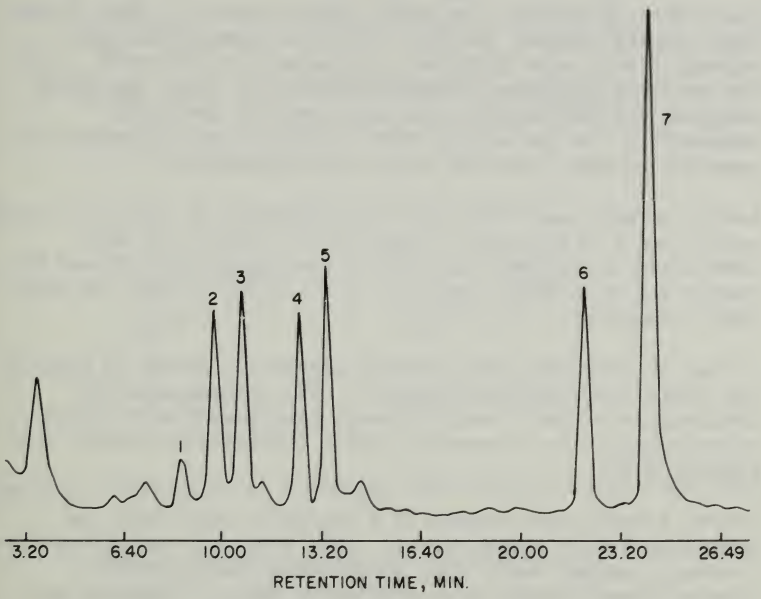

Figure 6.--Ether extract of $NaHCO_3$ solution of sugar A-1. Peak identities are listed in Table 5.

Table 5.--Compounds identified by CC/MS in the ether extract of a saturated sodium bicarbonate solution of sugar A-1

Peak No.	Compound
1	Diethylene glycol
2	Glycerol
3	Catechol
4	Resorcinol
5	Acetyl formoin
6	Unknown (73, 219, 45, 338, 297, 191)*
7	Unknown (73, 219, 45, 338, 191)*

*Numbers in paretheses refer to major ions in the mass spectral fragmentation pattern.

Compounds that Contribute to Caramel Flavor

Apart from sweetness, the major flavor impact of light brown sugar is its caramel flavor. Compounds responsible for caramel flavor were difficult to isolate and identify. All the extracts possessed powerful caramellic odors but GC/MS analysis did not always yield any compound obviously responsible for the strong odor. However, two compounds of powerful caramel odor and flavor were identified.

Acetyl formoin was identified in an extract of sugar A-1, and maltol was a major peak in sugar E-2. Maltol was also identified in extracts of 1 kg of coating syrups E-1 and E-2, indicating that these compounds are usually present in very small quantities.

A list of compounds with caramel flavors is found in Table 6 and their structures in Figure 7. The common molecular features is a planar enol-carbonyl configuration of alkyl substituted 5- or 6-membered cyclic α-diketones (Ohloff and Flament 1978).

Acetyl formoin also exists in a straight chain form, as 3-hydroxy-2,4,5- hexanetrione. This compound, in addition to a strong caramel odor, also possesses a characteristic intense sweet buttery odor similar to that of diacetyl and 2,3-pentanedione. The structural similarities are quite obvious suggesting that there is a continuum in flavor from buttery (or butterscotch) to caramel. The compounds listed in Table 6 are browning products from acid, alkaline, or thermal degradation of carbohydrates.

Diacetyl has an odor threshold of 4 ppb in water (Ohloff 1978) and a flavor threshold of 29 ppb in milk (Reddy et al. 1969). We found that a 25% sugar solution containing 5 ppm diacetyl tasted intensely sweet compared to a control and had a pleasant flavor reminiscent of, but not identical to, caramel. We also found that 5 ppm diacetyl masked the flavor of 100 ppm acetic acid in 25% sugar syrup. Diacetyl was found in the volatile profile of all sugars and syrups examined, and undoubtedly contributes significantly to the flavor of brown sugar.

Bone Char as a Source of Flavor

Char washing possessed a distinct "char" odor, as did the light brown sugar produced using it (sugar B). As discussed in an earlier section, diacetyl, acetaldehyde, ethanol, and pentane were identified in this sweetwater by means of the external GC method. None of these compounds alone or in combination contribute to "char" odor. Unfortunately, this

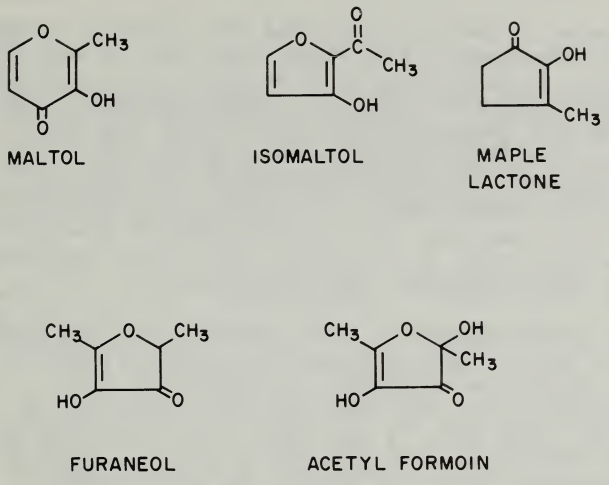

Figure 7.--Structure of compounds with caramel flavor and odor.

Table 6.--Compounds with caramel flavor

Common name	Structural formula
Maltol	2-methyl-3-hydroxy-4-pyranone
Isomaltol	3-hydroxy-2-acetylfuran
Maple lactone (Cyclotene)	2-hydroxy-3-methyl-2-cyclo-pentene-1-one
Furaneol	2,5-dimethyl-4-hydroxy-3(H)-furanone
Acetyl formoin	2,5-dimethyl-2,4-dihydroxy-3(H)-furanone

sample developed microbiological contamination and had to be discarded before an ether extract for TLC and GLC analysis could be obtained.

Ether extracts of freshly regenerated char possessed a strong odor, with characteristics of "sugar char" odor as well as nutty odors. A similar odor could be obtained by pyrolyzing zein, a corn protein. On GLC, the extract contained about 50 peaks. The only compounds identified at this time were pyridine, 2,6-lutidine (2,6-dimethylpyridine), and 2,4,6-collidine (2,3,6-trimethylpyridine). Lutidine and collidine both possess odors characteristic of bone char. Although these compounds have not been detected in sugars with a char-type odor, it is possible that their contribution to odor is due to extremely low concentrations.

Thin layer chromatography of these extracts developed many fluorescent spots. Ferric chloride spray showed that no phenolic compounds were present. Visualization with anisaldehyde/sulfuric acid spray produced a multitude of colors. One large spot, in particular, with a mobility of about 0.7, was extremely interesting in that it seemed to posses a typical "char" type of odor and went through a series of color changes on exposure to air, indicating high reactivity. Even without a visualizing spray, this spot oxidized on the TLC plate to a blue-green color. This spot was scraped off the plate and eluted from the silica gel with ether. Subsequent gas chromatography showed that this spot contained almost as many peaks as the original extract. No further attempt has been made to identify individual components.

Similar ether extracts of exhausted service char showed a different set of spots and none of the major spot described above, indicating that it had been removed during processing. New char also had this spot, but it was of lesser intensity than from regenerated char. We feel that the compounds extracted from regenerated char result from pyrolysis of sugarcane protein absorbed onto the carbon during decolorization.

When soft sugars from bone char refineries were extracted with ether and developed on TLC with the same conditions used for the bone char extracts, a large spot developed with visualizing spray that had the same mobility and flurorescence as the large bone char spot. The spot possessed some very faint "char" odor. However, it did not undergo the dramatic color changes as did the spot from the bone char, possibly indicating that oxidation had already occurred prior to extraction. The compounds in this spot may represent some of the bone char contribution to brown sugar flavor. We have not had the opportunity to examine soft

sugars made without bone char to confirm this finding, but all soft sugars examined possess this spot to a greater or lesser extent.

CONCLUSION

Many of the compound identified in brown sugars have strong, characteristic odors and flavors perceived at low concentrations. Table 7 is a partial list of some of these constituents whose food usage is established by the Food and Drug Administration and are generally recognized as safe (GRAS) (Furia and Bellanca 1975).

This is a varied list of compounds with correspondingly varied individual flavor contributions. A knowledge of the source of the different constituents is of some value in future attempts to control flavor. This information will be especially useful to refineries considering a change in process, and possible effects of the change on their soft sugars. Table 8 contains a summary of the sources of some flavor compounds. It can be seen that many are degradation products of metabolites from the sugarcane plant that go through the refining process.

In summary, we have begun to elucidate some of the factors that contribute to flavor in sugar and their sources. Differences in kind and quantity of constituents exist from sugar to sugar, which can account for flavor difference. This study has shown that there are objective, measurable differences in light brown sugars from different manufacturers, and thus from different processes. The correlation of formation of chemical compounds with process is expected to elucidate other chemical problems, particularly those associated with color formation and sucrose degradation and loss.

The next steps in this research are to determine how taste panels distinguish differences in sugars and to find the causes for some of these differences, quantify them, and relate them to sugar processing.

Table 7.--Established food usage and organoleptic qualities of some compounds identified in light brown sugars

Compound	FEMA No.*	Organoleptic qualities	Usage, ppm
Acetaldehyde	--	Fruity, green	3.9-270
Acetic acid	2006	Characteristic odor and taste	39-5900
Benzoic acid	2131	Sweet-sour to acrid taste; Odorless to faintly balsamic	4.8-250 (.1% preserv.)
Diacetyl (2,3-butanedione)	2370	Powerful, sweet, buttery or butter-scotch odor and taste	2.5-44
Furfural	2489	Penetrating, almond-caramel	0.8-45
Heptanal	--	Very strong, fatty, harsh pungent odor; fatty taste	1.2-4.9
Hexanal	2557	Characteristic fruity odor and taste on dilution	1.3-4.2
3-Hexene-1-ol	2563	Intense green odor and taste	1-5
Lactic acid	2611	Slightly sour odor and taste (Usage of 1200-24,000 ppm in pickles and olives)	14-300
Maltol	2656	Caramel	4.1-90
2-Methyl-butanal	2691	Powerful, choking odor; cocoa or coffee-like flavor when diluted; sweet, slightly fruity, chocolate-like taste	1.5-6.6
2-Methyl-3(H)-tetrahydrofuranone	3373	Sweet, faintly caramel; found in coffee and molasses	10.0

Pentanal (valeraldehyde)	3098	Powerful acrid pungent odor at low levels, a warm, nutty fruity taste	1.3-5.4
2,3-Pentane-dione	2841	Sweet odor similar to diacetyl	(usage not listed)
2-Pentyl furan	3317	Fruity odor; sometimes reported as licorice-like	3.0

*FEMA = Flavor and Extract Manufacturers Association

Table 8. Sources of Flavor in Brown Sugar

Compound	Type of Flavor	Source
Acetic acid	Acidic; part of the typical brown sugar flavor	Microbiological, found in sweet-water
Acetyl formoin	Desirable, caramel impact	Carbohydrate degradation
"Charred"	Undesirable if too concentrated	Bone char
Diacetyl	Desirable flavor, sweetness enhancer	Glucose pyrolysis, browning reaction product
Furfural	Caramel, nutty	Carbohydrate degradation
HMF	May contribute to bitterness or astringency if too concentrated (Maga 1979)	Acid carbohydrate degradation, leads to colorant formation
Heptanal, hexanal	Fruity to fatty flavors (See Table 7)	Degradation of long-chain fatty acids from sugarcane plant
3-Hexene-1-ol	Green, grassy	Sugarcane plant

Lactic acid	Found in most brown sugars; may enhance acidic notes	Microbiological
3-Methyl butanal 3-Methyl propanal	Found in all sugars; fruity, green flavors; harsh if concentrated	Strecker degradation of amino acids
Metallic	Undesirable, especially if highly concentrated or in ferrous form	Probably due to iron from equipment, acid corrosion, or rust
Pentyl furan	Can contribute to stale, licorice or cardboard flavor (Teranishi et al. 1971)	Linoleic acid degradation
Phenols and phenolic acids	Various flavors depending on structure, ranging from spicy-aromatic to smokey	May be metabolic breakdown products, many are colorant precursors

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DISCUSSION

R. RIFFER: In the ether extract of bone char did you analyse for polycyclic aromatic hydrocarbons? These are carbohydrate pyrolysis products and also potent mutagens and carcinogens.

M. A. GODSHALL: We have not identified all of the peaks; however we did identify pyridine and 2 methyl substituted pyridines.

R. RIFFER: Did you find any of another very important class of flavorants; condensation products of invert and amino acids?

M. A. GODSHALL: We did not find any of these in the char extracts. Browning products containing nitrogen are not very soluble in ether. Furaneol is the product of condensation between rhamnose and piperidine. However, I suspect that the process of regeneration would destroy these larger molecules. In the reaction the nitrogen is lost and is not contained in the final product. This compound was not found in our extract.

J. E. IRVINE: In your previous work you found dimethyl sulfide in molasses, but in Table 9 it is conspicuous by its absence. What happened to dimethyl sulfide?

M. A. GODSHALL: Dimethyl sulfide is not found in brown sugars. It is in edible molasses and in molasses from the raw mills. We have not looked at refinery molasses. Most raw sugars have a small amount of dimethyl sulfide, so we would probably find that it has concentrated in the molasses as it does in the raw end. We originally expected to find it in brown sugar, but this was not the case. Since it is also not found in brown sugars that have a high molasses content, another possibility is that the amount of dimethyl sulfide in the raw sugar, ie. the starting material, is low enough that most of it is lost in process by volatilization.

COLOR IN REFINERY PRODUCTS

Earl J. Roberts and Mary An Godshall

Cane Sugar Refining Research Project, Inc.

INTRODUCTION

In earlier studies in this laboratory the silica balance (Godshall et al. 1976) and polysaccharide balance (Roberts et al. 1978) have been followed through the refining process. Since removal of color is the principal reason for refining sugar, it seemed worthwhile also to follow the color in the refinery to determine both the removal and formation of color in the various processing steps. The color in the refinery products is the color not removed during clarification and decolorization plus that formed during refining. Because the turbidity in sugar solutions is usually included in the color measurements it was of interest to study some of the characteristics of this material, such as particle size, molecular weight range and composition. The term color in this report therefore includes any material which prevents the passage of light of 420 nm through a solution.

This paper describes a study of the color balance in three refineries in the boiling through the 4th strike; the isolation and identification of several color precursors and decomposition products of sugar which occured during refining; the results of our study of the particle size, molecular weight range and composition of the suspended material in solutions of refined sugar, and its effect on color measurements.

EXPERIMENTAL

Materials

Samples of No. 1 liquor, 1st sugar, 1st syrup, 2nd sugar, 2nd syrup, 3rd sugar, 3rd syrup, 4th sugar, and 4th syrup were obtained from each of three refineries. The refineries furnished the percentages of solids distributed between the

crystalline sugar and the corresponding syrup with each set of samples.

The operating procedures used by the refineries on the No. 1 liquors were as follows: Refinery 1, phosphatation, press filtration, bone char and granular carbon. Refinery 2, phosphatation, bone char and ion exchange. Refinery 3, phosphatation, bone char, and ion exchange.

The refined sugar samples were obtained from refineries or purchased at grocery stores.

Color Measurement

The refinery liquors and sugar solutions were adjusted to 50 Brix and to 7.0 pH. Color measurements were made by ICUMSA method 4 (ICUMSA 1974) as described below. The solutions were vacuum filtered through a mat of analytical filter aid on Whatman number 2 filter paper. After filtration the transmittance was read on the Talameter.

Extraction of Syrup with Chloroform

A sufficient quantity of 4th syrup (71 Brix) to contain 1000 g of solids was diluted to 50 Brix. The pH was adjusted to 2.5 with 2N sulfuric acid. The solution was then extracted in a separatory funnel with ten 100 ml portions of chloroform. The combined chloroform extracts were dried over sodium sulfate. The chloroform was removed and the residue was analyzed by thin layer chromatography (using toluene-ethanol-water-acetic acid (100:28.5:7.5:0.5)), gas chromatography, and mass spectrometry (Godshall *et al.* 1980).

Filtration of Refined Sugar Solutions

A 100 g sample of each sugar was dissolved in 100 g of water and the transmittance was determined without clarification or pH adjustment. Each solution was filtered successively through Millipore filters of 8, 5, 3, 0.8, and 0.45 micron pore size. After each filtration the color was determined in the filtrate.

Centriguation of Sugar Solutions

One thousand grams (1000g) of each sugar to be centrifuged was dissolved in 1000 ml water. The color was measured and the solution was centrifuged in small batches in stainless steel tubes at 40,000G for 20 minutes. The color of the centrifuged solution was measured. The sediment was transferred to a single tube and washed several times with 70% V/V alcohol to remove sugar. The sediment was dried, weighed and its

composition was determined as described by Roberts and Carpenter (Roberts and Carpenter 1975).

Dialysis of Sugar

One hundred grams (100g) of each sugar was dissolved in water, the volume was adjusted to 200 ml and the color was measured on the Talameter. The solutions were dialyzed in bags with molecular weight cutoff values of 12,000, 8000, and 3500 against flowing deionized water for 100 hours. The solution remaining in each bag was concentrated by ice sublimation to 200 ml and the color was measured on the Talameter.

DISCUSSION OF RESULTS

Color Formation

Color balance. The data furnished by the refineries on the distribution of crystalline sugar and syrup solids is shown in Tables 1, 2, and 3 along with the color found in each product.

Table 1
Color and Distribution of Solids Between Crystalline Sugar and Syrup

Refinery 1			
Sample	Color	Solids	Color
No. 1 Liquor	150	1st sugar - 55.6%	18
		1st syrup - 44.4%	309
1st Syrup	309	2nd sugar - 54.1%	35
		2nd syrup - 45.9%	666
2nd Syrup	666	3rd sugar - 53.7%	69
		3rd syrup - 46.3%	1266
3rd Syrup	1266	4th sugar - 51.7%	145
		4th syrup - 48.3%	2281

Table 2
Color and Distribution of Solids Between Crystalline Sugar and Syrup

Refinery 2

Sample	Color	Solids	Color
No. 1 Liquor	140	1st sugar - 52%	10
		1st syrup - 48%	278
1st Syrup	278	2nd sugar - 50%	21
		2nd syrup - 50%	554
2nd Syrup	554	3rd sugar - 48%	28
		3rd syrup - 52%	1232

Table 3
Color and Distribution of Solids Between Crystalline Sugar and Syrup

Refinery 3

Sample	Color	Solids	Color
No. 1 Liquor	134	1st sugar - 40.6%	17
		1st syrup - 59.4%	450
1st Syrup	450	2nd sugar - 42.5%	37
		2nd syrup - 57.5%	2420
2nd Syrup	2420	3rd sugar - 38.6%	79
		3rd syrup - 61.4%	4120
3rd Syrup	4120	4th sugar - 32.8%	148
		4th syrup - 67.2%	6266

The recovery of crystalline sugar by refineries 1 and 2 was slightly above 50% while that by refinery 3 was somewhat lower. It is observed in Table 1 that the yield of 1st strike sugar is 55.6% of the sugar in the No. 1 liquor and its color is 18 m.a.u. Since the 1st strike sugar represents 55.6% of the sugar available, it follows that 0.556 x 18 = 10,

represents the total color in the 1st strike sugar. In like manner 44.4% of the sugar remained in the 1st syrup and its color was 309 m.a.u. Then 0.444 x 309 = 137, the total color of the sugar remaining in the syrup. Then 10 + 137 = 147 represents the color associated with all of the sugar leaving the first strike and agrees well with the color of the no. 1 liquor. Therefore no color was formed during this strike. The color produced in subsequent strike was calculated in a similar manner. Tables 4, 5, and 6 show the color balance

Table 4
Color Balance - Refinery 1

	m.a.u. in	m.a.u. out	% change
1st Strike	150	147	-2.0
2nd Strike	309	327	4.9
3rd Strike	666	623	-6.4
4th Strike	1266	1176	-7.1

Table 5
Color Balance - Refinery 2

	m.a.u. in	m.a.u. out	% change
1st Strike	104	138	32.7
2nd Strike	278	287	3.2
3rd Strike	554	653	17.9

Table 6
Color Balance - Refinery 3

	m.a.u. in	m.a.u. out	% change
1st Strike	134	274	104.5
2nd Strike	450	1403	211.8
3rd Strike	2420	2560	5.8
4th Strike	4120	4258	3.3

in the samples studied. Inspection of the data in Table 4 shows that essentially no color was formed through the 3rd strike in sample 1. In samples from refinery 2, Table 5, variable amounts of color were formed, with color formation averaging 18%. The samples from refinery 3, Table 6, indicates that either considerable color was formed during the first two strikes or that dark liquor was recycled during the time the samples were collected. There was essentially no color formed during the 2nd and 3rd strikes.

Identification of Compounds in Chloroform Extract of 4th Syrup. The compounds indentified in the chloroform extract of 4th syrup are listed in Table 7. These compounds were identi-

Table 7
Compounds identified in 4th syrup

Maltol	Catechol
Acetic acid	4 Methylcatechol
Propionic acid	Isobutyric acid
Butyrolactone	N,N-dimethylformamide
Dimethoxy-methane	Furfuryl alcohol
Acetol	Valeric acid
Butyric acid	5-Hydroxymethyl furfural

fied by thin layer chromatography, gas chromatography, and, mass spectroscopy. Most of these compounds are decomposition products of reducing sugars and may be color precursors under refinery conditions. The remaining part of the sugar from which these compounds were formed probably condensed to make dark colored polymers when these decomposition products were forming.

COLOR AND TURBIDITY

Composition of Turbidity - Filtration.

The removal of apparent color by filtration of 50 Brix sugar solutions is shown in Table 8. The greatest amount of apparent color was removed by the filter of 8 micron porosity, ranging from 21% to 51% removal. This indicates that these particles are greater than 8 microns in size. Very little or no apparent color was removed by filters of 5, 3, and 0.8 micron porosity. The filter with porosity of 0.45 microns removed an average of about 20% more than the 8 micron filter. The material filtered out on the 8 micron and 0.45 micron filters was quite colored and was more soluble in water than in 50 Brix sucrose solution. The results are shown graphically in Figure 1.

TABLE 8
Color in Refined Sugar Before and After Filtration
Through Millipore Filters

Pore Size of filter-microns	Color - m.a.u. Sugar No.				
	I	II	III	IV	V
Original	79	152	54	45	122
8	51	137	26	36	96
5	51	134	25	34	96
3	51	125	23	34	93
0.8	48	121	21	33	86
0.45	45	105	18	32	83

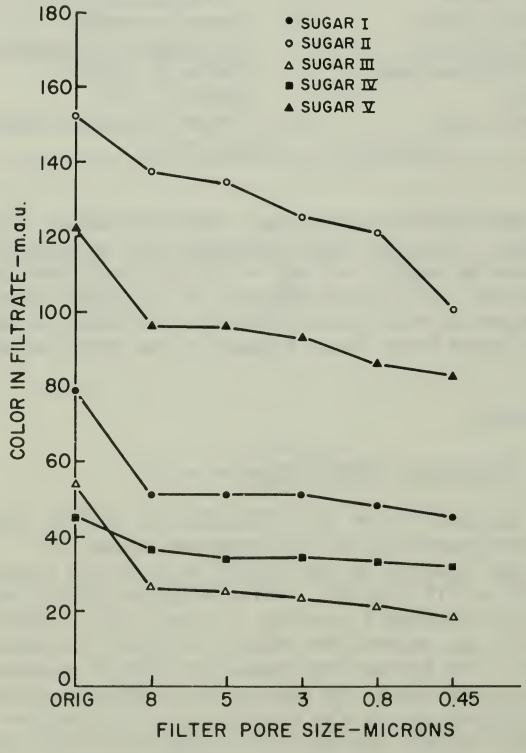

Figure 1. Color in Refined Sugar Before and After Filtration Through Millipore Filters.

Composition of Turbidity - Centrifugation

The results of centrifuging refined sugar solutions are shown in Table 9. Sugar 1 was a high grade refined sugar.

Table 9
Sediment separated from refined sugar solutions by centrifuging

Sugar	Sediment PPM	color removed %
Good	13	30
Poor	59	47

Centrifuging removed 30% of the apparent color with a corresponding weight removed from 1000 g of sugar of 12.8 mg. Sugar 2 was a commercial sugar with a high dextran content. In this case 47% of the color was removed by centrifuging. The weight of material removed by centrifuging 1000 g of sugar was 58.5 mg. The composition of the material removed by centrifuging is shown in Table 10. It will be noted from the

Table 10
Composition of sediment centrifuged from sugar solutions

Polysaccharides	Silica
Protein	Wax
Fats	Lipids

table that the composition of this material is similar to that of acid beverage floc from a qualitative standpoint. The polysaccharides are the major component and include indigenous sugar cane polysaccharide, starch and in most cases some dextran.

Composition of Turbidity - Dialysis.

The results of dialysis of sugar solutions is shown in Table 11. The first sample was a high grade sugar and 76% of the apparent color was retained in the bag of 12,000 molecular weight cutoff, indicating that 76% of the apparent color had molecular weight greater than 12000. In like manner 83% had molecular weight greater than 8000 while 94% had molecular weight greater than 3500. The second sample was a poor grade

Table 11
Results of dialysis of sugar solutions

MW Cutoff of bags	Sugar quality and color retained in bags - m.a.u.		
	good	poor	foaming
orig.	54	169	122
12000	41	157	57
8000	45	157	60
3500	51	167	64

commercial sugar with a high dextran content; 93% of the apparent color had molecular weight greater than 12,000, 93% greater than 8000 and 99% greater than 3500. The third sample was a refined sugar that gave foaming problems and 46% of the apparent color had molecular weight greater than 12,000, 93% greater than 8000, and 99% greater than 3500.

SUMMARY

Color formation was quite variable in samples from two of the three refineries. Therefore no conclusion can be drawn as to where most color was formed. Fourteen non-sugar constituents were identified in 4th syrup. Some of these are possible color precursors.

Filtration, centifugation, and dialysis of refined sugar solutions showed that 20% to 50% of the particles were larger than 8 microns, 46% to 93% of the particles had apparent molecular weights greater than 12,000, and 30% to 47% of the apparent color was removed by centrifuging at 40,000 G.

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DISCUSSION

H. R. PRIESTER: How were the yields shown in Tables 1, 2, 3 determined?

E. J. ROBERTS: The refineries furnished us those data and we don't know exactly how they were determined. I assume that they obtained valid figures. I wish we could have gone farther because there were more strikes. However, when unknown amounts of dark liquors were added back, that was the end of it as far as we were concerned.

E. D. GILLETT (Refined Syrups and Sugars): What was the history of the pan feed liquors? Had they all been polish filtered? Were they char liquors or granular carbon liquors?

E. J. ROBERTS: They had all gone through clarification and bone char decolorization. Maybe some of them were filtered after char, but I can't say for sure.

M. A. CLARKE: Will you give some details about the problems with foaming sugars?

E. J. ROBERTS: We have on several occasions received samples of sugar that foamed very badly in process. Some foam in the evaporators, some at earlier process stages. Some of the older literature leads you to believe that foaming is caused by alyophillic colloid which lowers the surface tension of the solution. It could be that a particular polysaccharide is the culprit. I can't confirm this at the present time.

L. A. ANHAISER (Imperial Sugar Co): In the tests on filtration could you tell us what was the criterion for starting with the 8 micron size. Did you try any other size before you settled on that one?

E. J. ROBERTS: Eight microns was the largest size we happened to have. We started with the largest and worked down as far as we could go and still get a finite rate of filtration.

A CASE STUDY OF COMPOSITIONAL AND QUALITY CHANGES IN RAW CANE SUGAR IN EXTENDED STORAGE

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BACKGROUND

The Food and Agriculture Act of 1977 mandated a loan or purchase program for sugar to support the price of sugarbeets and sugarcane during a time of depressed prices. A regulation implementing a sugar price support loan program was put into effect on November 8, 1977. Under this program processors of sugarcane and sugarbeets were able to borrow money (13.5 cents per pound for raw cane sugar, raw value basis) from Commodity Credit Corporation (CCC) by pledging sugar in storage as collateral. Processors could repay the loans at any time through the loan maturity date or could forfeit the sugar at the loan maturity date and keep the loan proceeds.

A total of 193,000 commercial tons of 1977 crop raw cane sugar were forfeited to CCC under the program, of which 145,000 tons were produced in Florida and 48,000 tons in Texas. The Florida sugar was moved from factory warehouses to a large warehouse in Jacksonville, Florida. CCC was able to arrange for extended storage of all the sugar forfeited in Texas at the factory warehouse in Santa Rosa.

At the time of forfeiture, raw sugar was selling well below the loan value and prospects for a significant improvement in price in the near future were dismal. Since CCC was not permitted to sell for less than 105 percent of the current loan rate, plus reasonable carrying charges, it appeared that the sugar acquired would be held in storage for an extended time.

A number of articles appeared in the media in the early months of 1979 expressing concern about CCC's growing stockpile of raw cane sugar and its cost to taxpayers. A newspaper article noted that raw sugar was never considered suitable for long-term storage. The sugar stored at Jacksonville was reported to be darkening and losing polarization. Sugar experts were

quoted as saying they had no way of knowing how much quality had been lost or the rate of further deterioration. In addition, there were rumors of serious deterioration and loss of raw cane sugar held in extended storage in the Philippines in recent years.

In the face of such disturbing reports, the stability of CCC's raw cane sugar became a matter of considerable concern to those responsible for the administration of the price support program. Instructions for sampling and testing the sugar were developed to determine whether the condition of the sugar was suitable for further storage. The instructions included detailed procedures for sampling sugar near the surface of the bulk storage piles in Jacksonville and Santa Rosa. In addition, an unprecedented project was undertaken at Jacksonville to sample sugar from borings made to points deep within the interior of the pile. All of the tests were made at the New York Sugar Trade Laboratory.

DESCRIPTION OF WAREHOUSES AND SUGAR IN BULK STORAGE

Santa Rosa, Texas

The raw cane sugar was stored in a typical "A" frame type sugar warehouse approximately 720 feet long by 166 feet wide. The sugar was piled upward at an angle of 37 degrees from 5 feet high retaining walls along each side length of the building. There were 48,000 tons of raw cane sugar in the pile which was 440 feet long, 160 feet wide and about 70 feet high.

Jacksonville, Florida

The sugar at this location was in a new warehouse which was not designed for storing raw sugar. The building was approximately 900 feet long by 280 feet wide. In most areas around the inside walls, sugar was piled upward from the bottom edge of the walls at an angle of about 37 degrees to the base of the floor. There were 145,000 tons of raw cane sugar in the pile which was about 32 feet high.

SURFACE SAMPLING AND TESTING AT SANTA ROSA, TEXAS

Sampling

The raw sugar was sampled every month at depths of 1 to 2 feet below the surface of the pile. A total of 21 samples were taken each month and consolidated into 7 composite samples each of which consisted of sugar from 3 samples. Dimensions of the pile and the locations at which samples were taken and composited are illustrated in Figure 1.

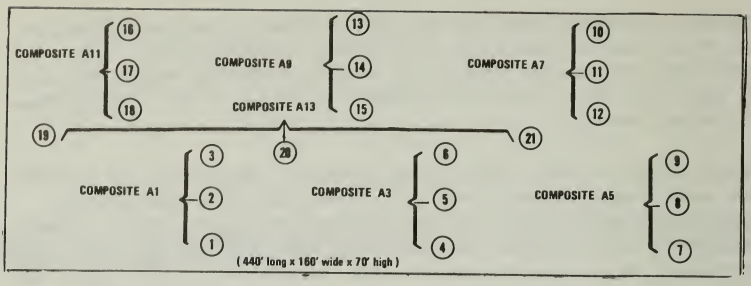

Figure 1.--Diagram of the raw sugar pile warehoused at Santa Rosa, Texas and the sampling and composite sample locations.

Each series of 3 samples included in composite A 1 through A 11 was taken approximately 140 feet apart along the side lengths of the pile. In addition, 3 samples were taken at midpoints across the width of the pile 140 feet apart and composited (composite A 13). All sampling locations were staked so that sugar could be sampled on succeeding months at points near the initial sampling locations.

Testing

Polarization and moisture tests were made on all composite samples each month. Color measurements and tests for invert sugar content were made on the initial series of samples and on those taken every third month thereafter.

Test Data

The test data (averages) obtained in monitoring the keeping and refining qualities of the raw cane sugar are set forth in Table 1. Each value is an average of tests made on 7 composite samples each of which consists of sugar from 3 samples.

The average of the Pol values for the last 3 months (November 1979-January 1980) in the tabulation is 97.83 which is slightly higher than the average Pol (97.77) of the sugar during the first 3-month period (March-May 1979) in which the condition of the sugar was followed. This 0.06 percent increase in Pol was accompanied by a slight decline in the average moisture content from a 0.46 percent average for the first 3 months to a 0.39 percent average for the last 3 months of storage. The apparent increase in Pol is due to the sugar drying out in storage. On the other hand, the decline in the moisture content is real and is directly responsible for the apparent increase in Pol.

Table 1.--Averages of tests on surface samples of raw cane sugar stored in bulk at Santa Rosa, Texas

Date Sampled	Pol	Moisture %	Invert Sugar %	Color* (ICUMSA units)	Safety Factor
3-23-79	97.78	0.50	0.26	225	0.23
4-30-79	97.77	0.44			0.20
5-28-79	97.75	0.43			0.19
6-15-79	97.81	0.42	0.28	241	0.19
7-17-79	97.75	0.53			0.24
8-14-79	97.84	0.48			0.22
9-14-79	97.86	0.42	0.26	252	0.20
10-15-79	97.89	0.40			0.19
11-16-79	97.74	0.38			0.17
12-17-79	97.96	0.31	0.29	260	0.15
1-15-80	97.79	0.47			0.21

*ICUMSA method 2 with light of wavelength 560 nm.

The test data indicate color levels in sugar trended upward during the storage period lowering the refining quality of the sugar. However, the rate of increase in color declined considerably with the onset of lower ambient storage temperatures during the fall months of 1979.

The Pol, moisture and invert sugar data indicate there has not been any significant change in the sucrose (Pol) content of the sugar in storage. All safety factors were in the safe range. The condition of the sugar was relatively stable during the 10 months of storage in all respects, except for color. At the end of the storage period, the sugar was still in good condition and suitable for further storage.

SURFACE SAMPLING AND TESTING AT JACKSONVILLE, FLORIDA

Sampling

The sugar was sampled about once a month at depths of 1 to 2 feet below the surface of the pile. A total of 44 samples were taken each month and consolidated into composite samples, each of which consisted of sugar from 4 samples.

The procedure followed and sampling locations at Jacksonville were similar to those described above for the raw sugar stored at Santa Rosa. For example, each series of 4 samples included in a composite sample was taken approximately 150 feet apart

along the side lengths of the pile. The first sample in each composite was taken at a point about 15 feet from the side wall. The other 3 samples were taken at locations upward toward the top or midpoint of the pile at right angles to the wall and in a straight line with the first sample location. The fourth sample was taken at the midpoint across the pile. All four sampling locations were spaced at equal distances. The same procedure was followed in obtaining samples for the other 10 composites. All sampling locations were staked.

Tests and Test Data

The tests made on composite samples, the frequency of testing and test results are given in Table 2. All of the test data (except for the January data) are averages of test results obtained on 11 composites, representing 44 samples. Due to shipments of raw sugar from the warehouse, the January data are averages of tests made on 7 composites, representing 28 samples.

The average of the Pol values from March 28 through August 2, 1979 is 98.59 which is only slightly higher than the average of the Pol values for the second 4-month storage period (98.56) extending from August 2 through November 28, 1979. There was virtually no change in the average moisture content of the sugar between these periods (0.235 percent average for the first 4 months versus 0.230 percent for the second 4-month period). The loss of 0.03 percent Pol between these successive 4-month storage periods is relatively small but may be significant. Color measurements increased from 103 ICUMSA units to 110 ICUMSA units with most of the increase occurring

Table 2.--Averages of tests on surface samples of raw cane sugar stored in bulk at Jacksonville, Florida

Date Sampled	Pol	Moisture %	Invert Sugar %	Color* (ICUMSA units)	Safety Factor
3-28-79	98.59	0.20	0.27	103	0.14
5-29-79	98.55	0.23			0.16
6-28-79	98.65	0.22	0.22	104	0.16
8-02-79	98.58	0.29			0.20
8-30-79	98.57	0.24			0.17
9-27-79	98.46	0.26	0.25	110	0.17
11-02-79	98.49	0.25			0.17
11-28-79	98.72	0.17			0.13
1-08-80	98.80	0.18			0.15

*ICUMSA method 2 with light of wavelength 560 nm

during the hottest summer months when the temperature of the air within the warehouse frequently exceeded 100 degrees F. Safety factors determined for the sugar were well within the safe range (0.25 or less).

These data indicated the sugar was holding up well in storage. At the end of 8 months of storage, the sugar remained in excellent condition and was suited for further extended storage.

CORE BORING, SAMPLING AND TESTING AT JACKSONVILLE, FLORIDA

Purpose of Core Boring Project

The purpose of core borings was to obtain samples of sugar at points deep within the interior of the pile which could not be reached by sampling near the surface. The object of this work was to obtain sugar samples at midpoints near to the bottom of the piled sugar and at other points deep within the interior of the bulk storage pile in order to determine whether the condition of the sugar was such that it could be stored safely for an extended period.

Drilling Locations

Instructions prepared for the contractor (Boring and Tunneling Company of America) called for horizontal borings to be made through door openings. The boring sites, the length of the bores (140 feet) and their direction are included in the diagram in Figure 2. All borings were made horizontally approximately 30 inches above the base of the warehouse floor.

Core Boring Operation

A boring machine mounted on a trailer was used to force 20 foot lengths of 3 1/2 inch diameter steel casing into the sugar. Augers (about 3 inches in diameter) were placed inside the casings for use in moving the sugar back to a discharge point on the trailer where the samples were taken. The front edge of the lead casing was flared upward to provide lift as the casing was extended through the sugar. This was done to offset the tendency of the casing to bend downward due to its weight and extended length.

An auger was placed inside each casing. A boring bit was fixed on the front end of the leading auger. The bit protruded out in front of the lead casing. The bit was rotated with the augers and served to loosen up the compacted sugar thereby facilitating the movement of sugar back through the casing as well as the advancement of the casing through the piled sugar.

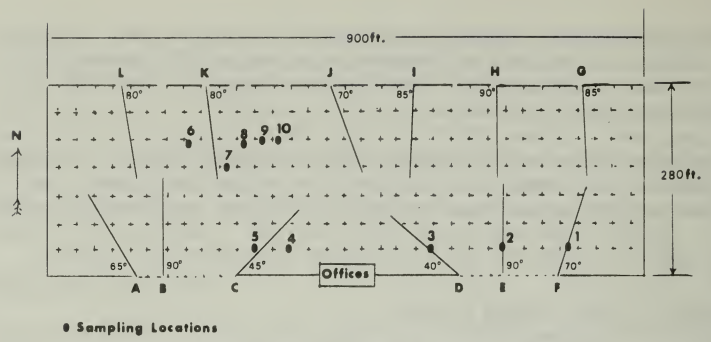

Figure 2.--Jacksonville boring plan.

After each 20 foot section of casing was forced part way into the sugar, the succeeding section was welded onto the end of the preceding casing. This procedure was repeated until there was a continuous 140 foot length of casing in the sugar at each boring location.

Core Sampling

Two grab samples of sugar were taken for every 10 feet of travel. One sample was taken for testing and the other sample, consisting of two large spoonfuls, was taken for use in making up a composite sample for the entire 140 foot length of each boring.

The grab samples taken for every 10 feet of travel were also placed in one-half gallon size glass jars with screw caps. The spaces between the edges of the caps and the jars were sealed with tape to prevent the transfer of moisture into or out of the sugar in the jars.

Visual Examination

All of the sugar obtained from the borings appeared to be in very good to excellent condition with the exception of sugar obtained at boring location K at depths between 110 and 130 feet. At the 110 foot depth, the sugar appeared to be darker with less attrition. In addition, the sugar appeared to have more molasses adhering to the crystals. This trend intensified for samples taken at 120 and 130 feet. Sugar sampled at 130 feet contained numerous balls and appeared to be very moist. Sugar augered at the 140 foot depth was normal in appearance. It should be noted, however, on visual inspection there was no evidence of deteriorated sugar obtained from any of the borings, as for example, by the presence of liquified sugar, fermented odors or the like.

Testing

In view of the favorable visual examinations made on sugar augered from the borings, it was decided to limit the testing to direct polarization and moisture determinations on 4 of the 14 grab samples taken for each boring. Three of these samples were selected at random and the fourth being the sample taken at the deepest point (140 feet) near the bottom and at or near to the midpoint across the pile. Due to the appearance of the sugar augered between 110 and 130 feet on K boring, five instead of the usual 4 grab samples were selected for testing for direct polarization and moisture content. Additional tests for invert sugar content were requested for sugar samples taken at 110 and 130 feet on that boring.

All 12 composite samples representing all of the sugar sampled on each boring were selected for testing for direct polarization, moisture, color and invert sugar determinations.

Test Results

Direct polarization measurements, moisture contents and safety factors for samples taken at varying depths on each boring are listed in Table 3. Test data for the core sample composites are tabulated in Table 4.

Table 3.--Pol and moisture test results on core samples of raw cane sugar

Boring location	Depth (feet)	Direct polarization (degrees)	Moisture (percent)	Safety factor
A	30	98.75	0.23	0.18
A	60	98.90	0.17	0.15
A	110	98.75	0.18	0.14
A	140	98.95	0.20	0.19
B	20	98.75	0.32	0.26
B	60	98.45	0.31	0.20
B	110	98.50	0.23	0.15
B	140	98.75	0.20	0.16
C	30	97.80	0.38	0.17
C	70	98.00	0.31	0.16
C	110	98.75	0.17	0.14
C	140	99.00	0.13	0.13
D	40	98.50	0.29	0.19
D	50	97.35	0.54	0.20

Table 3.--Pol and moisture test results on core samples of raw cane sugar--Continued

Boring location	Depth (feet)	Direct polarization (degrees)	Moisture (percent)	Safety factor
D	90	98.05	0.38	0.19
D	140	98.60	0.25	0.18
E	10	98.75	0.31	0.25
E	60	98.60	0.30	0.21
E	100	98.70	0.32	0.25
E	140	98.90	0.18	0.16
F	20	99.05	0.09	0.09
F	80	99.05	0.16	0.17
F	120	98.85	0.17	0.15
F	140	99.00	0.12	0.12
G	10	98.55	0.40	0.28
G	60	98.45	0.28	0.18
G	90	98.90	0.25	0.23
G	140	99.00	0.15	0.15
H	40	98.55	0.30	0.21
H	70	98.60	0.34	0.24
H	100	98.95	0.22	0.21
H	140	98.80	0.16	0.13
I	30	98.45	0.27	0.17
I	90	98.30	0.40	0.24
I	120	98.00	0.59	0.30
I	140	97.65	0.70	0.30
J	20	98.60	0.20	0.14
J	50	98.45	0.20	0.13
J	100	98.70	0.22	0.17
J	140	98.60	0.18	0.13
K	50	98.65	0.22	0.16
K	100	98.75	0.27	0.22
K	110	96.45	0.85	0.24
K	130	95.90	1.18	0.29
K	140	97.30	0.83	0.31
L	10	98.50	0.29	0.19
L	50	98.35	0.32	0.19
L	100	98.85	0.17	0.15
L	140	98.90	0.16	0.15

Table 4.--Test results on core sample composites[1]

Boring location	Direct polarization (degrees)	Moisture (percent)	Color (ICUMSA units)[2]	Invert sugar percent	Safety factor
A	98.75	0.19	196	0.24	0.15
B	98.60	0.23	217	0.22	0.16
C	98.30	0.29	192	0.29	0.17
D	98.15	0.38	188	0.27	0.21
E	98.65	0.31	240	0.17	0.23
F	98.90	0.15	223	0.20	0.14
G	98.70	0.27	198	0.20	0.21
H	98.60	0.32	204	0.27	0.23
I	98.55	0.41	244	0.25	0.28
J	98.70	0.23	157	0.24	0.18
K	98.05	0.43	231	0.60	0.22
L	98.65	0.22	206	0.25	0.16
Averages	98,55	0.29	208	0.27	0.20

[1]Each composite represents 14 core samples taken at 10-foot intervals to 140 feet.
[2] ICUMSA method 2 with light of wavelength 560 nm.

Boring locations B and G. Test data set forth in Tables 3 and 4 indicate that the condition of the sugar augered from the interior of the pile on B and G borings was very similar in a number of respects. For example, in both cases, sugar augered from the 20 foot and 10 foot depths on B and G borings, respectively was of high quality as indicated by the high polarizations (98.75 and 98.55 degrees, respectively). In addition, the sugar sampled at these locations had marginally to moderately high safety factors of 0.26 and 0.28, respectively. Tests made on all other samples taken from these borings had high polarization values (ranging from 98.45 to 99.00 degrees) with safety factors well below 0.25, ranging from 0.15 to 0.23.

The 98.61 degree average polarization of sugar augered from B boring at the 20, 60, 110 and 140-foot depths closely corresponded to the 98.60 degree polarization of sugar sampled at 10-foot intervals over the entire 140 feet of the boring which is listed for and represented by the composite for B boring location in Table 4. The average moisture content (0.265 percent) of samples taken at 4 depths specified along B boring is only moderately higher than the 0.23 percent moisture content of the composite sample.

Similarly, the average of the polarizations (98.72 degrees) obtained on sugar samples taken on G boring at the depths specified in Table 3 agrees closely with the 98.70 degrees polarization listed for the composite sample in Table 4. The average moisture content (0.27 percent) of the samples taken at the 4 locations noted along G boring is the same as that listed for the composite sample.

The invert sugar content of the composite samples for B and G borings (0.22 and 0.20 percent, respectively) are considered normal (low) and give no indication of deterioration in the sugar. Likewise, the color measurements (217 and 198 ICUMSA units) made on the B and G boring composites, respectively are satisfactory for raw cane sugar which had been in storage for approximately 2 years.

In view of these findings, it is apparent that the sugar with the marginally to moderately high safety factors is largely confined to areas near the side of the pile on the B and G borings near the 20 foot and 10 foot depths, respectively. This sugar is still of high quality and therefore will likely continue to store well for an extended period despite the 0.26 and 0.28 factors of safety. All of the sugar obtained at each of these boring locations is of high quality, in good to excellent condition and well suited for further storage.

Boring location I. Sugar sampled at the 30 and 90 foot depths is satisfactory in all respects. The sugar is of better than average quality (very good) with low factors of safety.

Sugar sampled at the 120 foot depth has the same moderately high safety factor (0.30) as sugar at the 140 foot depth. Their respective polarizations (98.00 and 97.65 degrees) are indicative of sugars of average and fair but below average quality. No evidence of deterioration was found in any of the sugar sampled from this boring. However, the quality and safety factor (0.30) of the sugar sampled at 120 and 140 feet are such that it is questionable whether some of the sugar sampled at these depths will remain stable in storage for an extended period of time.

The polarization of the composite sample (98.55 degrees) is substantially above the 98.10 degree average polarization of the samples taken at the 30, 90, 120 and 140 foot depths. This indicates that the 4 samples are not representative of the overall quality of the sugar augered from the entire length of the boring. Likewise, the moisture content of the composite sample (0.41 percent) is well under the 0.49 percent average for the 4 samples. These data indicate the quality and stability of the sugar augered from the I boring is substantially better than the sugar obtained in this boring at the 120 and 140 foot depths.

The invert sugar content of the composite sample is normal (0.25 percent) giving no indication of deteriorated sugar. The color measurement (244 ICUMSA units) is relatively high for raw cane sugars and is also higher than color measurements obtained on any of the other composite samples. However, this color level does not reflect a serious impairment to either the refining or keeping quality of the sugar.

The findings noted above and especially the test results reported for the composite sample provide the bases for our opinion that most, though possibly not all, of the sugar augered out of I boring would hold up well in storage over an extended period.

Boring location K. Sugar sampled at 50 and 100 foot depths along boring location K is of excellent quality with low safety factors, indicating the sugar sampled at these depths should store well. At the 110 foot depth, the polarization value dropped off sharply from 98.75 degrees at 100 feet to 96.45 degrees. However, this poor quality sugar had a satisfactory safety factor (0.24), indicating the sugar should hold up well in storage. At 130 feet there was a further drop off in the polarization of the sugar to 95.90 degrees reflecting very poor quality. The moisture content of this sugar was high (1.18 percent), and its safety factor of 0.29 is in the doubtful range. Due to the very low test of the sugar sampled at this depth and its relatively high safety factor, we could not be sure the condition of the sugar would remain stable over an extended period of storage.

The quality of the sugar sampled at the 140 foot depth improved substantially as reflected by the sharp increase in polarization from 95.90 degrees at 130 feet to 97.30 degrees at 140 feet. The quality of this sugar is considered fair though well below average quality of raw cane sugars. The 0.31 factor of safety determined for this sugar is in the doubtful range. In view of this, some portion of the sugar sampled at 140 feet on K boring may not hold well in storage.

As noted above, the sugar sampled at the 140 foot depth was normal in appearance. We believe the excessive moisture in the sugar sampled at 130 feet migrated into this sugar depressing its polarization and increasing its safety factor into the questionable range.

The 98.05 degrees polarization of the sugar on the K boring composite reveals the average quality of sugar along K boring is good and slightly above average for raw cane sugars. This polarization of the composite sample is substantially higher than the 97.41 degree average polarization for sugars sampled at the 50, 100, 110, 130 and 140 foot depths on this boring.

The 0.43 percent moisture content of the composite is well under the 0.67 percent average moisture for the 5 samples. In view of this, the quality of the sugar sampled at 50, 100, 110, 130 and 140 feet is not representative of the quality of sugar taken for every 10 feet of travel along boring K.

Invert sugar content (0.60 percent) of the K composite is more than twice as high as the invert sugar levels in the other boring composites. The higher level of invert sugar content together with the relatively low polarization value (98.05 degrees) of the K boring composite indicates there has been some destruction of sucrose (deterioration) in the sugar. Samples taken at 110 and 130 feet had invert sugar contents of 1.43 and 1.48 percent respectively.

The color intensity of the composite (231 ICUMSA units) is considered satisfactory for raw cane sugar. The safety factor (0.22) for the composite sample is in the satisfactory range.

In our opinion, much of the sugar taken from K boring would hold well in storage. However, both our visual observations and test data indicate the presence of a substantial pocket of sugar along this boring that is either of questionable or unsatisfactory keeping quality. There is nothing to indicate to us that the pocket of such sugar extends much beyond the 140 foot depth of the boring. On the other hand, the sharp improvement in the quality of sugar augered at 140 feet suggests that the pocket does not extend far beyond this point.

All other boring locations. Test data tabulated in Tables 3 and 4 for boring locations A, C, D, E, F, H, J and L indicate that sugar augered from each of these borings is excellent in quality and well suited for extended storage.

COMPARISON OF TEST DATA OBTAINED BY SURFACE SAMPLING RAW CANE SUGAR IN BULK STORAGE VERSUS SAMPLING FROM CORE BORINGS

In Table 5, there is a tabulation of direct polarization and moisture test results and safety factors determined for composite samples taken near the surface on November 2, 1979, while the core boring operation was in progress. The averages of these tests agree very closely with averages of corresponding tests and safety factors set forth in Table 4 for core sample composites from each of the 12 borings. There were no corresponding tests made for invert sugar content and color on the surface samples taken in November. The sampling procedure and testing instructions called for invert sugar and color tests to be made only every third month.

Table 5.--Pol and moisture test data on raw cane sugar sampled near the surface of the storage pile at Jacksonville, Florida on November 2, 1979

Composite Sample No.	Pol	Moisture (Percent)	Safety Factor
1	98.50	0.24	0.16
2	98.65	0.20	0.15
3	98.55	0.26	0.18
4	98.40	0.28	0.18
5	98.55	0.21	0.14
6	98.35	0.28	0.17
7	98.50	0.25	0.17
8	98.45	0.27	0.17
9	98.40	0.25	0.16
10	98.50	0.25	0.17
11	98.55	0.24	0.17
Averages	98.49	0.25	0.17

The most recent complete series of tests made on surface composite samples taken on September 27, 1979, are in Table 6. The test averages for the surface composite samples are also close to those obtained on core sample composites with the exception of color measurements. Color levels in the core samples were nearly twice as high on averages (208 ICUMSA units) than those in the surface samples (110 ICUMSA units).

Higher color levels in the core samples may have been caused by heat. Some heat resulted from the friction associated with the boring and augering of the sugar back through the steel casings. Another source of heat could have resulted from the leakage of water under the warehouse doors which was a regular occurrence following rain storms earlier in 1979.

Sucrose (sugar) readily reacts with water (hydrolysis) in acid solution (an aqueous solution of raw cane sugar is acidic) to form glucose and fructose at rates that increase steadily with increasing temperature and decreasing $_{p}H$. The dissolved sugar in rain water provided an excellent growth medium for bacteria, yeasts and molds. These microorganisms have enzymes which further catalyze the hydrolysis of sucrose to glucose

and fructose. Microbial growth increases the acidity of the medium and, thus further catalyzes the reaction. The chemical equation for the reaction is as follows:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{heat}]{\text{acids enzymes}} C_6H_{12}O_6$$

sucrose + water → glucose

$$+ C_6H_{12}O_6 + \text{Heat}$$

fructose

This destructive reaction is exothermic (gives off heat) in nature which is a factor of particular importance to a situation where water comes into contact with sugar piled in bulk storage. If, for instance, water seeped under the pile of sugar, the heat generated by the sugar reacting with the water would tend to accumulate within the pile, which would further catalyze the reaction and increase the rate of sugar destruction.

In order to determine the extent rain water had seeped back under the pile, sugar was removed by digging back from the edge of the pile to reach and sample sugar which appeared not to have been dampened by the seepage. Samples were taken on

Table 6.--Test data on surface samples of raw cane sugar in bulk storage at Jacksonville, Florida on September 27, 1979

Composite Sample No.	Direct Polarization (Degrees)	Moisture (Percent)	Safety Factor	Invert Sugar (Percent)	Color* (ICUMSA) units)
1	98.00	0.37	0.19	0.32	136
2	98.55	0.21	0.14	0.21	113
3	98.60	0.25	0.18	0.21	90
4	98.50	0.30	0.20	0.26	106
5	98.55	0.24	0.17	0.21	122
6	98.05	0.27	0.14	0.23	141
7	98.55	0.25	0.17	0.23	117
8	98.55	0.24	0.17	0.21	103
9	98.55	0.26	0.18	0.21	104
10	98.60	0.22	0.16	0.35	94
11	98.60	0.24	0.17	0.30	86
Averages	98.46	0.26	0.17	0.25	110

*ICUMSA method 2 with light of wavelength 560 nm

May 31, 1979, off the base of the warehouse floor at distances ranging from 1 to 2 feet back from the edge of the pile opposite warehouse doors. The samples were tested for direct polarization and moisture content. The results of these tests are in Table 7.

The average moisture content of 0.40 percent was nearly double the average moisture content of the surface samples (0.23 percent) taken on May 29, 1979, (Table 2). The average polarization (98.16 degrees) was substantially less than the average polarization of the surface samples (98.55 degrees) indicating that some of the sucrose content in the sugar had broken down. In other words, there was evidence of deterioration in the sugar. Test data (averages) obtained on surface samples in the course of monitoring the condition of CCC raw cane sugar at Jacksonville, Florida are set forth in Table 2.

A second series of samples was taken on July 5, 1979, after digging further back into the sugar opposite doors in an attempt to determine the extent of seepage of rain water under the pile of sugar. Samples were taken off the base of the warehouse floor between two and three feet back from the edge of the pile with the exception of the sample taken opposite Rail Door No. 12. Due to the high percentage of moisture (1.39 percent) and low polarization (92.45 degrees) of the sugar sampled by this door on May 31, 1979, this sample was taken after removing sugar approximately 5 to 6 feet back from the side edge of the pile. Test data reported for these samples are also tabulated in Table 7.

The average moisture content of the samples (0.50 percent) is more than twice the average level of moisture in surface samples taken on June 28, 1979 (Table 2). Also, the average polarization (98.37 degrees) is significantly less than the 98.65 degree average polarization of surface samples taken on June 28, 1979. The average moisture content (0.50 percent) is also substantially higher than the 0.40 percent average of samples taken opposite doors on May 31, 1979. Accordingly, it was apparent that more rain water had seeped under the sugar pile between May 31 and July 5, 1979.

No further attempts were made to determine the extent of water seepage by digging up and removing sugar back from the edge of the pile. Time, expense and problems associated with digging back into and setting aside sugar taken from increasing depths made further digging into the pile practically impossible.

Table 7.--Test data for raw cane sugar sampled at Jacksonville, Florida on May 31 and July 5, 1979 to determine the extent of damage due to leakage of rain water under warehouse doors

Door		Pol		% Moisture	
		May 31, 1979	July 5, 1979	May 31, 1979	July 5, 1979
Personnel	1	99.00	98.85	0.24	0.32
Personnel	2	98.55	97.05	0.34	0.91
Personnel	3	98.40	98.70	0.45	0.41
Personnel	4	98.40	98.50	0.46	0.55
Personnel	5	98.55	98.45	0.31	0.41
Truck	1	98.90	98.25	0.27	0.44
Truck	3	98.75	98.30	0.19	0.56
Truck	5	98.65	98.70	0.37	0.42
Truck	7	98.55	97.85	0.36	0.62
Truck	9	98.30	98.60	0.26	0.39
Truck	11	98.40	98.35	0.41	0.56
Truck	13	98.30	98.20	0.53	0.49
Truck	15	98.35	98.70	0.42	0.38
Truck	17	98.55	98.30	0.24	0.61
Truck	19	98.30	98.50	0.30	0.47
Truck	21	98.55	98.70	0.22	0.38
Truck	23	97.60	98.30	0.37	0.44
Rail	1	98.25		0.46	
Rail	2		98.05		0.73
Rail	4	98.20	98.50	0.39	0.47
Rail	6		98.50		0.51
Rail	8	98.45	98.45	0.39	0.37
Rail	10		98.55		0.53
Rail	12	92.45	98.55	1.39	0.54
Averages		98.16	98.37	0.40	0.50

After CCC had sold the sugar and after some of it had been loaded out away from the sides of the warehouse, written authorizations were obtained from the new owners to take additional samples to determine the extent of the water seepage and the cause for increased color intensity in sugar sampled from the core borings. Special sampling instructions were developed which called for the sugar to be sampled near the edge of the pile as closely as possible to each of the 12 boring locations noted in the boring plan diagram in Figure 2 above. However, the removal of sugar by pay loaders had resulted in cliffing (i.e. the sides of the sugar which had compacted and hardened in storage were relatively vertical

rather than at the 37 degree angle of repose when the loose sugar was loaded into the warehouse). Some of the sugar which was at the top of the cliffed pile tended to break away and drop off to the bottom of the pile. At most core boring locations, avalanching of sugar from the top sides of the pile precluded sampling sugar which was originally placed at those locations when the sugar was loaded into the warehouse. In view of this, samples had to be taken at the side edge of the pile at points where the sugar had not avalanched down from the top sides. Samples were taken on April 8, 1980 at 10 locations along the north and south sides of the sugar pile. The sampling points are marked in the boring plan diagram (Figure 2). The sampling locations ranged from 40 to 120 feet back from the side walls of the warehouse.

At each sampling location, separate samples were taken off the base of the floor and 30 inches above the base of the floor (core boring height). In addition, separate composite samples were prepared, representing sugar sampled at all of the 10 locations at floor level and core boring height.

Samples taken at 6 of the 10 locations and both composite samples were selected for testing for direct polarization, moisture content and color. Test data reported to us by the New York Sugar Trade Laboratory are set forth in Table 8.

Table 8.--Results of special tests made to determine causes of the higher color intensity in sugar sampled from core borings

Sample	Sampling locations: Floor	Sampling locations: 30" above floor	Distance from wall (feet)	Pol	Moisture (percent)	Color* (ICUMSA units)
1-B	X		40	90.50	3.67	106
1-T		X	40	97.55	0.31	157
3-B	X		40	89.25	2.94	122
3-T		X	40	97.15	0.58	149
5-B	X		40	92.50	1.62	102
5-T		X	40	99.00	0.12	134
6-B	X		80	89.00	2.49	105
6-T		X	80	99.00	0.16	139
7-B	X		120	87.75	2.92	119
7-T		X	120	99.15	0.11	142
10-B	X		80	82.20	4.28	166
10-T		X	80	99.10	0.12	172
Composite	X			90.25	2.63	115
Composite		X		98.55	0.25	144

*ICUMSA method 2 with light of wavelength 560 nm

The direct polarization and moisture test data obtained on the samples taken at floor level disclosed that the seepage of rain water carried far back under the piled sugar. Sampling locations on the south side of the pile were 40 feet back from the south wall to which the sugar pile had originally extended. Sampling locations along the north side of the pile were 80 to 120 feet back from the north wall.

The water caused considerable destruction of sucrose in sugar as evidenced by the very low polarization values, ranging from 82.20 to 92.50 degrees on samples taken at floor level. This sugar was in a highly deteriorated condition which may account for the relatively low color (115 ICUMSA units). Some of the pigmented decomposition products originally formed by the decomposition of sucrose may have in turn broken down which would account for the loss of color in the floor sample composite.

The polarization of the composite sample at the core boring height (98.55) is in exact agreement with the polarization of samples taken from the core borings (98.55) and in close agreement with the polarization of surface samples (98.49) taken while the core boring operation was in progress. Therefore, there is evidence that the sugar piled at core boring height did not come into contact with the rain water seepage.

The moisture content of the sugar sampled at core boring height (0.25 percent) is in exact agreement with that of the surface samples taken on November 2, 1979, during the core boring operation and in close agreement with the level of moisture in the core samples (0.29 percent). Thus, absorption of moisture was not a factor in sugar piled 30 inches above the base of the floor.

The color intensity of the composite sample (144 ICUMSA units) taken at core boring height is much higher than that found in samples of sugar taken at the surface (110 ICUMSA units) on September 27, 1979, but considerably lower than the 208 ICUMSA units of color found in the core samples. In view of this, it appears that the heat resulting from the destruction of sugar at floor level is directly responsible for much of the color increase found in core samples and the remainder of the added color in core samples may have resulted from heat due to the friction of augering the sugar back through the steel casings.

DISCUSSION

The deterioration of raw sugar is brought about principally by the action of microorganisms and their enzymes. Two important factors in this regard are the number and type of microorganisms and the moisture content of the sugar.

Raw sugar consists of a crystal of nearly pure sucrose surrounded by a molasses film. All of the microorganisms and virtually all of the moisture are contained in the molasses film. Consequently, the molasses film is the site of microbiological activity which leads to deterioration and loss of sugar in storage.

Fortunately, the high osmotic pressures of highly concentrated solutions, such as molasses (about 80 degrees Brix), retard the growth of microorganisms. Bacteria do not play an important role in sugar deterioration for such organisms are unable to survive in solutions where the Brix exceeds 65 degrees whereas some yeasts and some molds are able to survive and propagate themselves in solutions of much higher concentration. In view of this, osmophilic yeasts and osmophilic molds constitute the primary threat to the stability of sugar in storage.

Data obtained by the Colonial Sugar Refining Company of Australia in studying sugar deterioration indicated that a sugar would be liable to deterioration during storage when the moisture content appreciably exceeds the nonsugar content. A correlation was found between the moisture and nonsugar contents to the keeping quality of sugar. This led to the development by the company of the so-called "factor of safety" which serves as an indicator of the probable keeping quality of a raw cane sugar. The underlying basis for these findings, including the safety factor, is the phenomenon that the growth of microorganisms is retarded by high osomotic pressures of high density solutions.

The factor of safety represents the ratio which the percentage moisture content of a sugar bears to its nonsugar content (100 - Pol). The term "safety factor" is widely used and understood in the sugar industry. Nevertheless, the term is misleading in that higher factors of safety are associated with increasing susceptibility of the sugar to deterioration. A more appropriate term would be "deterioration factor."

If a raw sugar has a safety factor of 0.25 or less, microorganisms cannot breakdown and metabolize the sugar and thus the sugar is considered safe for storage. It is not considered safe to store sugars with safety factors above 0.33.

Safety factors above 0.25 up to and including 0.33 are considered to be in a doubtful range. In other words, it is questionable whether all of the raw sugar in a particular batch or lot or within a warehouse with safety factors within this range would be suitable for extended storage. In this regard, it is important to keep in mind that the safety factor, in a sense, represents an average value obtained on a sample that hopefully is representative of a particular lot and in no way reflects the variable composition of sugar within the lot.

Limits established for safety factors are based on molasses of 80 degrees Brix adhering to the raw sugar crystals. Although molasses produced in a factory may average 80 degrees Brix or more for an operating period (10 days to 15 days) or perhaps, even on a daily basis, it is important to realize that the Brix solids in molasses vary appreciably from strike (batch) to strike.

Accordingly, it is quite possible for some portion of a lot of raw sugar with a safety factor in the doubtful range to have adhering molasses of less than 80 degrees Brix. Such sugar would be subject to spoilage even though it is part of a batch or lot of raw sugar whose crystals are coated with a molasses whose Brix average 80 degrees or higher. In essence, each grain of raw sugar is a case unto itself.

Safety factors in the range (above 0.25 up to and including 0.33) are considered questionable in order to take into account such variability in the solids content of molasses. Therefore, it follows that all of the raw sugar in a lot with a safety factor in the doubtful range is not susceptible to spoilage. However, the possibility exists that some portion of the lot may be threatened with spoilage due to variable Brix levels in molasses resulting from the crystallization of sugar on each boiling (strike).

SUMMARY AND CONCLUSIONS

Tests made for Pol, moisture and invert sugar content on raw sugar sampled near the surface of the bulk storage piles at Jacksonville, Florida and Santa Rosa, Texas indicate very little, if any, significant change in the sucrose (Pol) content of the sugar during 10 months of storage. The test data reveals that the sugar was very stable in storage. There were, however, significant increases in color measurements made on the sugar in storage at both locations. Color levels in the sugar stored at Jacksonville increased from 103 to 110 ICUMSA units in a 6-month period. The color intensity in the sugar stored at Santa Rosa increased from 225 to 260 ICUMSA units over a period of 9 months. These data indicate the sugar held up well in storage and that its condition was such that it was considered suitable for further storage.

Both visual inspection and test data indicate that sugar withdrawn from 8 of the 12 borings to be of excellent quality and in condition suitable for further storage. Findings made with regard to sugar sampled from borings B and G are quite similar. For example, sugar with questionable safety factors sampled from borings B and G seems to be limited to small pockets near the sides of the pile at these sites (20 foot and 10 foot depths, respectively). In both instances the polarization values of the sugar in question are high. In view of this, these high quality sugars are likely to hold well in

storage despite their questionable safety factors. All other sugar sampled and tested from borings B and G was of excellent quality and satisfactory in every respect for further storage.

Likewise, findings made on sugar withdrawn from borings I and K have much in common. In each case, sugar with questionable factors of safety was situated at points deep within the pile, ranging from 120 to 140 feet.

Sugar with questionable safety factors on I boring was of fair to good quality. It is doubtful whether some of the sugar taken at the 120 and 140 foot depths will hold well in storage. However, most of the sugar from this boring is expected to store well over an extended period.

Much of the sugar taken from K boring is also expected to hold up well in storage. There is, however, a pocket of sugar along this boring that is either of questionable or unsatisfactory keeping quality. Some part of the sugar in this pocket, particularly that at the 130 foot depth, is not expected to remain stable in storage for an extended period due to its very poor quality (95.90 degrees polarization) and questionable factor of safety (0.29).

Tests indicated a marked improvement with regard to the storability of the sugar at the 140 foot depths on I and K borings. However, in view of the relatively poor quality of the sugar at these depths and their doubtful safety factors, it is considered questionable whether some part of this sugar will be stable in storage over an extended period.

In all instances, findings noted in this report indicate that pockets of sugar with questionable factors of safety are relatively small in size and for the most part limited to a small span (length) along 4 of the borings. The great bulk of the sugar was of excellent quality and should hold well in extended storage provided proper storage conditions are maintained.

Direct polarization and moisture determinations made on samples composited from locations near the surface of the pile of CCC raw cane sugar warehoused at Jacksonville, Florida agreed closely with such determinations made on samples composited from core borings made to points deep within the interior of the pile. However, color measurements made on core samples were nearly twice as high on average (208 ICUMSA units) than those made on surface samples (110 ICUMSA units).

Higher color levels in the core samples are attributed to heat generated by the hydrolysis of sucrose (Pol) in sugar brought about by rain water running under the warehouse doors into

contact with the sugar and the seepage of the water far back under the piled sugar. Another factor contributing to the higher color intensity in core samples was the heat resulting from the friction of augering the sugar out from the interior of the pile through steel casings.

DISCUSSION

P. PETRI (Audubon Sugar Inst.): Would you do anything different in the future in sampling the surface of the pile?

J. A. HUPFER: In the title of our paper, we noted that it was a case study. The sampling procedures were developed for sampling sugar near the surface of the bulk storage piles at Jacksonville and Santa Rosa. However, I would not recommend that what was done at those locations should necessarily be repeated someplace else. For instance, a similar plan was developed for sampling 5 warehouses in Puerto Rico. Tests made on the samples disclosed that the composition and quality of the sugar varied considerably within each of the bulk storage piles. Fortunately, the sugar was sold a short time after the initial sampling. But, had the sugar been held much longer, we would have modified the procedure in view of the high degree of variability in the composition and quality of the sugar.

F. G. CARPENTER (Southern Regional Lab.): Did you measure any temperatures in that hugh pile of sugar?

J. A. HUPPER: Yes we did. I might add that when we did the core boring, we left the casings in the pile with the idea of running thermistors through them so that we could monitor the temperature of the sugar within the pile. In addition we had recording thermometers in place within the warehouse in the airspace at several locations. But the really important temperature was the temperature of the sugar within the pile. We dug down into the sugar and inserted thermistors. The highest temperature at a depth of 4 to 5 feet in the middle of the summer was 80°F. The temperature was not a matter of great concern to us at that level. But if the temperature had risen to about 100°F we would really have been concerned.

M. A. CLARKE: How much did this endeavor cost? I refer to costs of the sampling and boring study, warehousing costs, freight costs in moving the sugar and other storage and shipping costs.

J. A. HUPPER: The core boring work alone cost about $40,000. In addition there were costs in terms of man hours spent by our personnel in taking samples of the sugar and in performing related tasks such as purchasing sample containers and shipping boxes. There were also costs for shipping the samples to the laboratory and laboratory testing fees. I don't have a total

cost figure for this work. The cost would, however, be relative small when considered in the light of CCC's 54 million dollar investment in the sugar and the time it was held in storage.

M. C. BENNETT (Tate and Lyle): Would one of the South African delegation care to comment about those enormous sugar stores in Durban?

M. MATIC: I think that what you have found here is correct. Sugar keeps very well when stored in a large pile as long as it is not too wet. Would you know whether this sugar before storage was dried or not, because here in Louisiana, for example, sugar is not dried.

J. A. HUPFER: The moisture content was very low. Most of the sugar in the warehouse was from Gulf and Western and from Sugar Cane Growers Coop of Florida.

E. ARIAS (Sugar Cane Growers Coop of Florida): The sugar in Florida is not dried in any type of equipment specifically for drying. We do use slingers to put the sugar in the pile and that constitutes some drying.

M. MATIC: Once moisture in the sugar is sufficiently low as indicated by the safety factor, long storage would be very easy. At least we found it easy in South Africa and I suppose that Australian experience is similar.

A STUDY OF CHEMICAL ADDITIVES FOR USE IN SUGAR REFINING

Richard Riffer

California and Hawaiian Sugar Company

INTRODUCTION

In our current decolorization system we use an average of 0.02% P_2O_5 on sugar solids and achieve 25-35% color removal in our raw liquor clarifiers. The Clarified Raw Liquor is then passed over bone char, which results in 80-90% color removal from the liquor entering char. Part of the dark fraction of No. 1 Liquor from bone char is passed over granular carbon, where we average 55-60% color removal over a long cycle.

Currently we are proceeding with detailed engineering of an ion exchange resin project which will be a major addition to our decolorization system. Resin will accomplish most of the decolorization for our granulated sugar.

At various times we have considered a number of chemical additives for supplementary color removal. More recently we have studied these in greater detail. A number of reagents were examined for possible use in the refining process, for control of color and turbidity, and for waste treatment. With some of these additives, extensive testing was carried out over a period of months. In other cases, fewer experiments were performed, more with the purpose of acquiring a better understanding of mechanisms of color and turbidity removal than with any view toward a direct practical application in the refinery. Our findings are reported here.

HYDROGEN PEROXIDE

Mechanism: Cleaves unsaturated sites and diketones in colorants, forming carboxylic acids. Oxidizes phenolics to quinones and acyclic products.

The reaction of peroxide with colorants is a fast one at typical refinery operating temperatures. In addition to its direct bleaching action, there is some evidence that peroxide also oxidizes certain colorants to forms that are more readily

removed by adsorbents. Both pH-sensitive and -insensitive colorants are reactive toward the reagent.

The color reduction observed upon treatment of various liquors is reported in Table 1. Liquor pH drops upon treatment as a result of acid formation. Raws that are poorly decolorized by peroxide are generally also resistant to decolorization by char and ion exchange resin. However dark liquors do not necessarily contain refractory colorants.

Table 1.--Decolorization with Hydrogen Peroxide

Liquor	% H_2O_2	% Decolorized
Remelt Liquor	0.03	24
Remelt Liquor	0.15	37
Remelt Liquor	0.30	73
Remelt Syrup	0.05	9.6
Remelt Syrup	0.20	19
Clarified Raw Liquor		
color >900	0.03	24
color <800	0.03	7.1
av. 25 samples	0.03	14
	0.15	26

SODIUM HYPOCHLORITE

Mechanism: Same as hydrogen peroxide.

Hypochlorite was found to be a much more effective decolorizer than peroxide, typically reducing Clarified Raw Liquor color by 60% at the 0.03% level of active chlorine, and 80% at the 0.06% level. However there are some serious difficulties with hypochlorite use, which are elaborated upon below. Hypochlorite appears to oxidize largely the same colorants as are adsorbed by bone char.

Hypochlorite exists only in alkaline solution, being converted upon acidification to free chlorine gas:

$$ClO^- + Cl^- + 2H^+ = Cl_2 + H_2O$$

Chlorine is in equilibrium with volatile hypochlorous acid:

$$Cl_2 + H_2O = H^+ + Cl^- + HClO\uparrow$$

Although the equilibrium constant is only 4.5×10^{-4} at 25°C., chlorine can be continuously converted to replenish hypochlorous acid lost to the atmosphere. Hence hypochlorite treatment of acidic solutions is wasteful of chlorine. Calcium

hypochlorite is a much less effective decolorizer than the sodium form, probably because of its lower solubility.

Hypochlorite was tested on liquors darker than Clarified Raw Liquor as well. Darker liquors required proportionately more hypochlorite: a remelt syrup sample, about ten times as dark as Clarified Raw Liquor, required about thirty times as much active chlorine to achieve a similar reduction (60%) in color. Remelt liquor color was reduced 47% by 0.07% active chlorine.

Colorant was fractionated by gel filtration on Sephadex G-10, and the fractions were subjected to hypochlorite treatment. The highest molecular weight fractions exhibited the greatest decolorization per unit of hypochlorite added. The lower molecular weight fractions initially consumed hypochlorite at constant color, and thereafter displayed low levels of decolorization as more reagent was added. However since low molecular weight colorants are generally present in much lower concentration by weight than high molecular weight, the fraction of the former destroyed by treatment could nevertheless be greater than that of the latter.

The high molecular weight fractions had darker initial colors than those of low molecular weight, but the equilibrium constant so overwhelmingly favors the products that initial colorant concentrations are irrelevant. We demonstrated that there is no advantage in treating dark liquors in preference to lighter ones by experiments performed with variable concentrations of sugar-free colorant added to sucrose-type liquid sugar. Of course certain darker liquors, such as remelt syrup, contain colorants different from those in raw liquor and less reactive toward hypochlorite.

Hypochlorite appears to attack preferentially color that tends to boil into the crystal. Thus our syrup from the fourth boiling was unreactive toward hypochlorite, but syrup from the third boiling was moderately reactive. Liquors not decolorized, such as blanched cane juice and evaporator syrup from the Hawaiian Islands, can nevertheless consume hypochlorite, which must preferentially oxidize colorless species. Likely candidates here are aldehydes and amino acids, particularly cysteine and methionine. These would be largely absent in later refining stages. Thus decolorization by hypochlorite is more effective after clarification, which appears to remove selectively colorless reducing non-sugars.

Clarified Raw Liquor was titrated with hypochlorite to an end point at which all susceptible colorants were considered to be oxidized; starch--iodide was used as indicator. The end point corresponded to 0.09% chlorine. At low levels of hypochlorite, Clarified Raw Liquor turns reddish; as more reagent is added, the color fades. A similar red color can be produced by such oxidizing agents as ferricyanide and ferric ion, which suggests

that phenolics react in a two-step sequence. They are apparently first oxidized to colored ortho-quinones, which are then cleaved to acyclic products. Similarly colorless hydroxyketones could be oxidized to colored diketones (which form highly colored ferric complexes) and subsequently cleaved.

Hypochlorite can reduce pH-sensitivity: the indicator value (pH 9 color/pH 4 color) of a sample of highly pH-sensitive granulated sugar was reduced from 11.4 to 3.2 by 0.06% chlorine. A fluorescent impurity disappeared at 0.07% chlorine. Clearly the effect of hypochlorite on indicator value would depend upon the colorant profile of the sample being treated, but phenolic color appears to be especially reactive.

Hypochlorite was also tested for color control of ion exchange waste streams, although we have found that most of the color in spent regenerant is biodegradable. Residual hypochlorite would have to be destroyed by sulfur dioxide before subsequent treatment in a digestion plant, because it is a powerful bactericide. On the other hand, hypochlorite-treated waste does not appear to be particularly toxic to wildlife: all fish survived in static acute toxicity ("fish bioassay") tests with treated waste diluted to our average bay-line concentration.

There is some evidence that carboxylic acids formed as a result of hypochlorination can catalyze new color formation during boiling, even after neutralization. Furthermore, hypochlorinated liquors are poorly decolorized by resin, bone char, or cationic polymers. Bleaching could result in the formation of highly polar colorless species that are preferentially picked up by hydrophilic adsorbents, leaving fewer sites for remaining colorants.

Small molecules formed by oxidative cleavage would also be expected to diffuse to adsorption sites much more rapidly than bulkier solutes. We found that hypochlorite treatment reduced the absolute value of the zeta potential of Clarified Raw Liquor by about 50%. Our zeta potential measurements are mean values, which are not as informative as probability distributions. However residual colloidal material appears to have a reduced charge density, which would hinder removal at hydrophilic surfaces (but facilitate removal by flocculation).

Hypochlorite treatment after strong base resin produces a yellowing believed due to residual phenolics. These could be luteolin derivatives, for which resin has a lower capacity than does bone char (Kennedy and Smith 1976). Again the effect can be simulated by mild oxidizing agents and appears to have a free radical mechanism.

We have not studied possible sugar loss by oxidation or the formation of chlorosugar by-products, which could be toxic or mutagenic. Any chlorinated organics that form would be

expected to be removable by carbon treatment. Glucose would be readily oxidized by hypochlorite (E^o = 0.94), since this is accomplished even by such mild agents as cupric ion (E^o = 0.167).

CATIONIC SURFACTANTS

Mechanism: Form insoluble adducts with colorants and other high molecular weight anionic impurities.

A four-month laboratory study indicated that addition of 500 ppm of cationic surfactant A to our phosphoric acid--lime defecation gave an additional 10-15% color removal to provide an overall color removal of 40 to 45%. The additional decolorization appeared to be relatively insensitive to raw liquor color. The additive also effectively reduced color remaining after resin treatment of Clarified Raw Liquor.

In our secondary waste treatment plant (BOD), we found that sludge resistant to settling could be made to floc at pH >7 with alum and cationic surfactant, or at pH <7 with alum and anionic polyelectrolyte. The net charge on settleable solids becomes more negative with increased pH. However cationic additives are effective on both acidic and alkaline sludges, since their isoelectric point is considerably lower than 7.

ALUM

Mechanism: Hydrolyzes to form alumina gels which have a large surface area for entrapment of impurities.

Laboratory studies indicated that 500 ppm of alum added during raw liquor defecation gave an additional 10-15% color removal over defecation alone, even with liming to a pH more alkaline than the alumina isoelectric point, above which positively-charged polymeric species are transient (Grutsch and Mallatt 1977). In the laboratory the coagulum was removed by filtration, but in a refinery gelatinous alum sludges would be difficult and costly to dewater.

Polyvalent cations such as aluminum are so effective at zeta potential reduction that this is accomplished at very low concentrations. Consequently the bulk of the alum added in our experiments must be utilized in colloid entrapment and not for zeta potential control. In fact, the amount of alum is so great in relation to the amount of potentially "entrappable" colloidal matter that the nature of the latter material is probably not relevant (Grutsch and Mallatt 1977).

Primary waste station (our settleable solids station) influent was made to settle rapidly and thoroughly in laboratory tests by the addition of alum. For a digester sludge sample of low settleability from our secondary waste treatment plant, the

older the sludge the greater was the settling effect of adding alum and polymer. The implication was that filamentous organisms such as Flexibacter and Thiotrix predominated and were interfering with settling and compaction (Sezgin et al. 1978). Such organisms, which have a high negative zeta potential, are known to be abundant in our activated sludge during periods of bulking.

POWDERED ION EXCHANGE RESIN

Mechanism: Adsorbent.

Laboratory tests were performed using 0.25% of powdered resin B (wet weight as supplied) on Clarified Raw Liquor and on a dark fraction of our No. 1 Liquor. An agitation/contact time of 9-10 minutes at 70-80°C. was used to simulate a refinery operation. The 0.25% figure is a typical level for powdered carbon when used as a primary decolorizer. In control samples we used this level of powdered carbon C, which is an effective one for treating sugar liquors.

We found that powdered resin dispersed well in high density sugar liquors and that it performed significantly better than powdered carbon (Table 2). However powdered resin is considerably more costly than carbon.

Table 2.--Powdered Resin as a Decolorizer

	% Decolorized
Clarified Raw Liquor	
powdered resin	32.3
powdered carbon	23.8
Dark fraction of No. 1 Liquor	
powdered resin	40.9
powdered carbon	29.2

COMMERCIAL FORMULATION D

Mechanism: The composition of D is proprietary. According to the manufacturer, it is formulated to remove color, ash, and turbidity from sugar liquors when used in conjunction with an anionic polyelectrolyte, E.

Decolorization tests were carried out on Clarified Raw Liquor and on a light fraction of No. 1 Liquor using two levels of additive (Table 3).

Table 3.--Formulation D as a Decolorizer

	% Decolorization	
	CR Liquor	No. 1 Liquor
50 ppm D + 5 ppm E	11.8	2.4
300 ppm D + 30 ppm E	47.6	11.6

Treatment did not result in a detectable turbidity reduction when the additive was tested on the light fraction of No. 1 Liquor.

NATURAL AND SYNTHETIC POLYAMIDES

Mechanism: Adsorbent, especially for phenolic color.

Milk casein and egg albumin were among the polyamides examined, since they are relatively inexpensive and have favorable isoelectric points. Casein was an especially attractive prospect because of its high content of calcium phosphate; it was hoped that this would facilitate incorporation into the growing coagulum during defecation. Casein and albumin were used in Persia and Egypt as early as 1,400 years ago for purifying sugar solutions (Spencer and Meade 1945).

The additives were used in conjunction with defecation, on raw liquor and on a light fraction of No. 1 Liquor. Color was not consistently improved, probably because of poor contact: the polyamide powders tested were all difficultly dispersed in liquor.

Polyamide as a scavenger for phenolics could be a useful supplement to decolorization in refineries using ion exchange. Resin does a poorer job than bone char in removal of phenolic color, so refined sugar from a resin refinery would tend to have a somewhat higher proportion of such color than that from a char refinery (Kennedy and Smith 1976). We have performed some tests on resin effluent using columns of another polyamide, pelletized Nylon 66T, which has FDA approval for contacting food. Decolorization was poor, probably because of the relatively small surface area: thin-layer chromatography grade polyamide performed well in laboratory columns.

BISULFITE

Mechanism: Adds to unsaturated carbonyl groups (Royals 1954) and certain flavonoids (Jurd 1964), resulting in a shortened resonance path in affected chromophores.

Bisulfite at the 500 ppm level reduced the color of Clarified Raw Liquor by only 4.5%. The thermodynamics and kinetics of the addition are unfavorable except for a small group of carbonyl compounds.

HYDROSULFITE

Mechanism: Reducing agent for diketones, phenolic colorants, and iron complexes. (Bisulfite is a reaction product which can subsequently add as described above.)

We found hydrosulfite to be a powerful decolorizing agent; at the 500 ppm level, Washed Raw Liquor color was reduced 37%, Clarified Raw Liquor 31%, remelt liquor about 36%. Higher levels of additive resulted in only small further improvements. However much of the color is slowly recovered by air oxidation. Furthermore, reducing agents containing sulfur are reportedly destructive toward ion exchange resins (Moody and Thomas 1972). For these reasons, treatment should be late in the refining process.

If the mechanism suggested above is correct, hydrosulfite after hypochlorite should result in greater decolorization than hypochlorite alone, but not with treatment in the reverse order. This is what is observed. The additional decolorization should be indicative of concentrations of quinones and iron complexes. The oxidative cleavage from hypochlorite treatment is irreversible, but iron present would be oxidized to the ferric state, which forms intensely colored complexes with residual phenolics and β-diketones. Ferric ion, and diketones and phenolics not cleaved by hypochlorite, could be reduced by hydrosulfite to less highly colored forms. Both ferric and ferrous iron form a catechol complex, but only the former is colored, probably because of its unpaired 3d electron, absent in the ferrous complex (Gould 1955).

PHOSPHATE

Our raw liquor is clarified using 0.02% P_2O_5 on sugar solids. In laboratory studies we found that doubling the level of phosphoric acid improved color by 19% and turbidity by 14%. However a corresponding increase could not be tested adequately in the refinery because the large floc volume interfered with clarifier scum handling.

Phosphatation of remelt liquor at the 0.02% level of P_2O_5 resulted in 19% decolorization; at the 0.04% and 0.10% levels, decolorization was 24% and 27%.

UREA

Mechanism: Disrupts hydrogen bonds, such as those linking colorant to sucrose. Also believed to cause unfolding of high

molecular weight colorants, to expose functional groups tied up by internal bonding.

In very limited testing, we found that urea slightly improved color removal during defecation. A greater increase in indicator value was observed than that from normal defecation, which suggested improved removal of high molecular weight color.

Thiocyanate behaves similarly but also forms an intensely colored complex with traces of iron.

CITRATE, EDTA

Mechanism: Complexing agents.

Our previous work with hydrosulfite had indicated that iron complexes with catechols and similar compounds such as maltol contribute substantially to the color of Clarified Raw Liquor. We found using model compounds that these complexes can be decolorized by competitive complexing agents such as EDTA or citrate (when [citrate]/[catechol] ≥ 5). Calcium competes with iron for the complexing agents, but citrate and EDTA are effective even when [calcium]/[iron] = 20, as can be found in sugar liquors. Fructose forms such a weak iron complex that it cannot compete successfully with catechol. The experiments were conducted in pH 7 buffer.

Lactate and aconitate, like citrate, form stable iron complexes that are much less intensely colored than the catechol complex. These were not tested as decolorizers for the iron/catechol adduct.

If not for its toxicity, fluoride would be a good choice here. The affinity of fluoride for iron is so great that it will even discharge the intense red color of the thiocyanate complex that is used as a sensitive qualitative and quantitative test for ferric ion (Cotton and Wilkinson 1972).

Our refinery water supply is fluoridated, so one might expect that fluoride would be available to complex a portion of the iron in our liquor and thus make it unavailable as a color contributor. In fact, iron levels in the water supply are just high enough to tie up all of this fluoride so that essentially no excess is available.

ASCORBATE

Mechanism: Reducing agent.

Ascorbate decolorizes iron complexes with catecholic non-sugars by reduction of iron at pH <7. However fairly high levels of

ascorbate are required to decolorize Washed Raw Liquor significantly, so costs are prohibitive.

ANIONIC DETERGENTS

Mechanism: Reduces positive zeta potentials; decreases entropy of system.

The addition of 500 ppm of sodium lauryl sulfate to clarified liquor resulted in a sharp increase in pH 7 color. The micellar system formed is believed to prevent colorant molecules from associating and also to make them more rigid (Humphry - Baker et al. 1980). Reagents which increase the structural flexibility of colorants or promote association should reduce the color level.

Such association should be favored at increased concentration. Thus when colorant is diluted, the absorbance should be reduced somewhat less than is calculated on the basis of concentration alone. This is what was found in experiments on sugar-free molasses colorant. (Since the colorants are for the most part weak acids, one would expect deviations from the Beer-Lambert law on the basis of ionization equilibria. For this reason the experiments were conducted in pH 4 buffer of constant concentration, to suppress ionization.)

ADDITIVES FOR TURBIDITY CONTROL

Enzymes. Dextran is commonly an important contributor to light scattering in sugar solutions. We found dextranase enzyme to be highly effective for turbidity reduction, both when added batchwise and when immobilized, using glutaraldehyde, on alkylamine porous glass beads and on phenol-formaldehyde resin.

Unfortunately dextranase does not have FDA approval for food use; the United States appears to be one of a small number of industrialized nations where its use is restricted. However we found in laboratory tests that an FDA-approved enzyme, α-amylase, catalyzes the hydrolysis of α-1$\rightarrow$6 linkages in dextran at a rate about 0.1 that for α-1$\rightarrow$4 linkages in its normal substrates, amylose and amylopectin. We achieved turbidity reductions of 40% in 5.5 hours using 250 ppm of enzyme on solids. Although such high enzyme concentrations would clearly be impractical for use on a throw-away basis, the study suggests that immobilized α-amylase could be of value for treatment of high purity liquors.

The Michaelis constant for the reaction of α-amylase with dextran is not known, but the enzyme would not be expected to have a high affinity for this glucan. The observed reaction rate was dependent upon dextran concentration (that is, not zero-order), which implied that the rate was not in the maximum region of the Michaelis-Menten curve.

Inhibitors. The best approach to the dextran problem, of course, is preventing its formation. We conducted a bacteriological study to determine under what conditions dextran formation might be inhibited.

A culture of Leuconostoc mesenteroides was obtained from the Department of Microbiology and Immunology at the University of California at Berkeley. Using this culture as a starter we prepared a set of additional cultures in agar and from these, sterile sucrose-free nutrient broths were inoculated to provide a relatively high concentration source of Leuconostoc. These in turn were used to inoculate sterile 13.0° Bx sucrose broths, which were then incubated at 30°C. for 18.5 hours. At the end of this period, the samples were sterilized in an autoclave to quench any further microbiological activity.

Various additives were introduced before inoculation to determine whether dextran formation could be inhibited. The additives tested were 100 ppm of bisulfite, 25 ppm of cetyl trimethylammonium bromide (CTMAB), and 2 ppm of fluoride. Bisulfite is widely used as a disinfectant. CTMAB is a cationic detergent which forms an adduct with the anionic bacterial cell wall and also denatures cell-membrane proteins. Fluoride at the 2 ppm level has been reported to inhibit dextran (plaque) formation in the oral cavity by disrupting the metabolism of Streptococcus mutans (Jenkins 1959, Jenkins et al. 1967). Of course the major benefit of dietary fluoride arises not from its disinfectant properties but from its incorporation into dentine hydroxyapatite.

After 18.5 hours the control samples had become viscous and highly turbid. Neither fluoride nor bisulfite had any discernible inhibitory effect, but the samples treated with CTMAB remained clear and showed no evidence of dextran formation. This suggested that dextran levels in raw sugar could be reduced by washing the cut cane free of soil and trash with water containing low levels of quaternary ammonium compounds such as CTMAB. This of course assumes rapid and good harvesting practice in the field.

Cationic detergents. Dextran in sugar liquors is intimately associated with dextransucrase, the bacterial enzyme that catalyzes its synthesis (Robyt et al. 1974). The dextran forms as an intracellular slime layer, and although this coating is easily sheared from very young bacteria, large amounts of the glucan tend to accumulate around the cells as the bacteria age (McKinney 1962).

Except at low pH bacterial cells have a negative surface charge, which is probably reduced by shielding in the encapsulated organism but cannot be entirely absent if metabolic processes are maintained. In high density liquors the cells are dehydrated, but the surface charge would be expected to persist in the

shrunken membrane. Thus dextran in raw sugar is partially removed by treatments dependent upon electrical charge, such as defecation and adsorption on bone char.

[To the degree that dextran adsorption on bone char occurs at hydroxyapatite sites, an analogy can be drawn with dental plaque dextran, which is strongly adsorbed onto dentine hydroxyapatite. Materials which are anticariogenic in the oral cavity, when present in sugar liquors might be expected to interfere with dextran removal on bone char. For example, since phosphate is anticariogenic (Harris 1970, Madsen 1970), one might expect dextran to be removed with difficulty by char from high-phosphate liquors. We have found that raws that cause the greatest turbidity problems also contain the highest levels of inorganic phosphate. Of course these raws are also high in polysaccharides.]

We have had limited success with removal of dextran by treatment with 500 ppm of CTMAB followed by defecation. Other cationic additives and alum also showed some activity. Using this technique we were able to achieve substantial (30-40%) reduction in the turbidity of washed raw, Clarified Raw Liquor, and light fractions of No. 1 Liquor. However large fluctuations in performance were observed, possibly due to variable levels of other polysaccharides. (1→6)-Homoglucans such as dextran are more difficult to remove than other polysaccharides because extra degrees of freedom provided by rotation about C-5 to C-6 bonds result in higher entropies of solution (Whistler 1973). This can be seen by examining molecular models.

Local differences in refractive index at the colloid-solvent boundary contribute to light scattering. Zeta potential reduction without defecation would be expected to increase turbidity by promoting increased association of solute molecules. The resulting colloidal aggregates would have reduced surface area in contact with the solvent.

Oxidants. According to Rayleigh's law, for particles smaller than 0.05λ (such as dextran) the intensity of scattered light is proportional to the sixth power of the scattering particle radius (Beyer 1969). Thus even a small reduction in radius should significantly reduce turbidity. The effect would be greatest for molecules in a rigid-rod conformation and least for spherical molecules. Polysaccharides are usually somewhere between these extremes, behaving as random coils or flexible chains (Everett and Foster 1959, Whistler and Smart 1953).

We found that turbidity could be reduced by oxidative cleavage of polysaccharides. We performed a set of experiments in which samples of a light fraction of our No. 1 Liquor were treated at 50° Bx and 70°C. with several levels of oxidants. After cooling, the samples were neutralized, and the turbidities and colors were read (Table 4). The average particle radius of

gyration was computed from the observed turbidity, on the assumption that the turbidity reduction was due solely to particle degradation. Molecular weight reduction was also estimated: for a random coil (but not for a rigid rod), the radius of gyration is proportional to the square root of the weight-average molecular weight (Everett and Foster 1959).

Periodate cleavage was not studied. The reagent is far too expensive to be considered for a refinery process.

Table 4.--Turbidity Reduction by Oxidate Cleavage

% Cl as ClO^-	Turbidity Coleman Units	Color $1000a^*_{420}$	Relative average radius of gyration	Relative weight-average MW
0	22.0	45.8	1.00	1.00
0.02	16.8	42.7	0.96	0.92
0.04	11.4	35.3	0.90	0.81
0.06	11.7	35.0	0.90	0.81
% H_2O_2				
0.02	18.3	45.5	0.97	0.94
0.04	11.4	29.0	0.90	0.81
0.06	11.7	27.3	0.90	0.81

We found that light scattering can also be reduced by pH adjustment, although this technique is of limited value. Polysaccharides containing glucuronic acid or other anionic components would be expected to assume more compact globular conformations of reduced light scattering capacity at lowered pH. Non-sugar colloidal matter behaves similarly, as we found in viscosity studies on colorants (Freeland et al. 1979).

Ultrasound also degrades dextran (Basedow and Ebert 1974 and 1975, Berg et al. 1960, Ebert et al. 1970, Zaretskii et al. 1971), but we did not have the facilities to test this adequately. According to literature reports, inhomogeneous flow fields stretch the helical structure, which is then cleaved into two approximately equal parts by a shock wave.

CONCLUSION

A review of cane sugar refining in the Cane Sugar Handbook (Carpenter and Clarke 1977) states that bleaching type decolorizers such as hydrogen peroxide, hypochlorite, and sulfite do

not remove colorants but only camouflage them. It has been our experience that oxidizing agents such as peroxide and hypochlorite permanently destroy color. To the degree that the mechanism is by oxidative cleavage of unsaturated sites, it is difficult to see how colorant could be reformed readily from the reaction products. Addition of sulfite to unsaturated carbonyls is certainly subject to reversal, as is reduction by hydrosulfite. However the use of the term camouflage was unfortunate, because it implies that the absorbance curve is hidden under a new curve (which would require a net increase in color) or that the original curve is temporarily distorted. To the extent that sugars bleached by oxidants do not have good keeping qualities, we believe that this is due to catalysis of new color formation by reaction products, but not reappearance of the original colorants.

Table 5 offers a brief summary of the performance of materials tested in this study. We are not using any of these additives at the Crockett refinery, but further tests are being conducted, including various combinations of additives. The potential number of permutations might seem astronomic, but in fact relatively few of the additives offer the prospect of synergistic or even complementary activity.

Table 5.--A Summary of Additives Studied

	waste treatment	phenolic color	non-phenolic color	iron complexes	zeta potential control	micro-organisms	turbidity
Hydrogen Peroxide		+	+			+	+
Hypochlorite	+	+	+			+	+
Cationic surfactants	+		+		+	+	+
Alum	+		+		+		+
Powdered resin		+	+				
Commercial formulation D		+	+				
Polyamides		+	+				
Bisulfite		+	+				
Hydrosulfite		+	+	+			
Phosphate		+	+				+
Urea			+				
Citrate, EDTA				+			
Ascorbate				+			
Anionic detergents					+	+	
α-Amylase							+

In these studies we limited ourselves for the most part to reagents which are FDA-approved for food use or for which there seemed to be a reasonable chance for such approval. However the FDA must be petitioned even for approved additives when these are to be used in a new application (except for GRAS substances - Generally Recognized as Safe). A proposal for hypochlorite treatment would be expected to come under close scrutiny; although chlorine is used to treat virtually every municipal water supply, in recent years low levels of chlorine-containing carcinogens have been identified in drinking water. Likewise hydrogen peroxide was reportedly carcinogenic in a Japanese study, even though this substance if found widely in living systems (background: 0.1 ppm).

Some additives and techniques were not examined because of cost considerations and obvious impracticality. For example, many high molecular weight polysaccharides (but not pure dextran) are strongly antigenic and could in theory be removed by adsorption on immobilized antibodies. However one would probably not care to use this technique to treat 3,800 tons of sugar per day.

The possible introduction of a chemical additive in our process ultimately depends upon cost effectiveness. Ideally one would like to have an inexpensive, safe, FDA-approved additive that can be introduced easily and in low concentration but that nonetheless results in a large improvement in color that is permanent and which produces no pollution or disposal problems, no sugar loss, and no difficulties in refinery operation. Such additives are clearly quite rare.

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DISCUSSION

C. C. CHOU: You mentioned the use of hydrogen peroxide and said that color was permanently destroyed by this reagent. This means that the color in the sugar would not reverse back during storage. Do you have any experimental data to support that?

R. RIFFER: No, I don't. However, there was no evidence of color recovery in treated liquors. Rather few of these liquors were boiled into sugars.

M. CHO (Audubon Sugar Inst.): When you add various chemicals to the sugar, how do you handle the removal of excess chemicals, specifically oxidizing agents?

R. RIFFER: Generally you have considerable amounts of reducing agents present in addition to colorants, so at the point at which color is no longer removed, the oxidizing agents will be consumed by other reducing agents, such as reducing sugars and even sucrose. In the laboratory one can use an indicator such as starch-iodide to find if there is an excess of oxidant.

M CHO: Since this is a food process, we have to be sure that the added chemicals are eventually reduced to zero. That is an important point to think about.

R. RIFFER: In the case of oxidizing agents you can always add a reducing agent to destroy the excess. You will find that most biological systems contain a certain amount of hydrogen peroxide, which gives a fairly high background and you will never be sure that you have removed all that you've introduced. You won't be able to distinguish added peroxide from naturally present peroxide.

M. A. CLARKE: When you used amylase instead of dextranase and found about 10% of the dextranase activity, that low activity could be because there are α-1$\rightarrow$4 linkages in the dextran that are similar to the linkages in starch that amylase attacks.

R. RIFFER: I am not so sure about that. There was some work done at Iowa State Univ. (Robyt et al, 1974) in which they found that there was actually hydrolysis of the other α-1$\rightarrow$6 bonds as well. α-Amylase is a relatively unspecific enzyme. (See J.J. Marshall, Adv. Carbo. Chem. and Biochem. 30, 286 (1974)).

M. A. CLARKE: How pure was the enzyme? Either dextranase or amylase could be contaminated with other enzymes.

R. RIFFER: I don't know. However highly purified preparations of α-amylase are readily obtainable, unlike the case for dextranase.

R. KUNIN: Enzymes have been treated rather academically as too expensive or associated with FDA problems. It appears to me that isomerase has never been examined carefully by FDA. It just went through with nobody paying much attention, so it should not be that much more difficult to approve an enzyme that occurs naturally for treating dextran. Another thing is that isomerase was not very effective until people studied how to promote its activity. Each enzyme needs an activator. The original activator for isomerase was cobalt, but that was frightening, so calcium and magnesium were used. A lot of work went on in the development of isomerase to improve its effectiveness and economy. I don't think this amount of effort has yet gone into the enzymes for dextran. If dextran is such a problem, then immobilization and adequate studies on optimization of its activity are potential areas for further research.

S. CLARKE (Audubon Sugar Inst.): In the oxidation with hypochlorite did you find any increase in gluconic acid which should be formed from the oxidation of glucose?

R. RIFFER: No, we did not test for this, but the glucose should be very easily oxidized if any were present.

S. CLARKE: So, as you increase the quantity of hypochlorite, you would have a competing reaction between oxidizing glucose and the decolorization.

R. RIFFER: Yes, that is right.

S. CLARKE: In the use of alum (aluminum sulfate), do you anticipate any problems in the formation of sulfate scale later in the process?

R. RIFFER: This could be a problem, but on the other hand, if you were using ion exchange resin in the chloride form later on, it would pick up all the sulfate.

S. CLARKE: Concerning the powdered ion exchange resins, ion exchange can't be used economically unless unless it is recovered and reused. How about that problem?

R. RIFFER: There are some indications that powdered ion exchange can be used economically on a throw away basis. This is something Dr. Kunin is going to talk about tomorrow.

S. CLARKE: The intensity of scattered light is proportional to the 6th power of the scattering particle radius. In forming particles by the addition of alcohol, do you expect different dextrans to form the same size particle to make the same haze?

R. RIFFER: I would expect higher molecular weight dextrans to have higher light scattering power.

E. MULLER (Tate and Lyle): You mentioned that addition of calcium chloride before bone char was beneficial. Can you give any idea of the concentration one has to use and how much improvement you get?

R. RIFFER: I have worked on this only a little, and at 500 ppm of added calcium chloride, I was getting improvements in decolorization over bone char of 30 to 40 %.

F. G. CARPENTER (Southern regional Lab.): The explanation can be found in Proc. Tech Sess. Bone Char for 1961. The polyvalent anions are preferentially adsorbed on bone char before colorant and block a colorant adsorption site. Their deleterious effect can be nullified by matching them with a polyvalent cation, in this case calcium. The polyvalent ion pair then either reverts to a condensed phase someplace else or the calcium re-establishes the colorant adsorption site one layer up. The amount required is that the polyvalent anions should not exceed polyvalent cations by more than about 1 millinormal concentration unit. The effect can be spectacular. In terms of color remaining after bone char, a change of 5 millinormal units can effect the color by a factor of 5. Fortunately, most sugars do not have excess polyvalent anions, but for those that do, the effect of a little added calcium chloride can be dramatic. A few refiners check the excess polyvalent anions and take advantage of this effect on a regular basis.

SOME SPECULATIONS ON SUGAR CRYSTALLIZATION

Andrew VanHook

College of the Holy Cross

INTRODUCTION

The rate at which sucrose crystallizes from any particular syrup is observed to pass through a maximum as the temperature is changed. This is illustrated schematically in Figure 1 using the data of Smythe (1971) for pure solutions.

The pattern is the same with the compilations of Kucharenko (1928), the writer (1958) and others. It is presumably unaltered for synthetic syrups as well as natural juices although it may be considerably subdued. This feature of both cane and beet juices has been well known for many years but there is a sparsity of published data.

The maxima in these or closely related curves are obviously critically definitive to the yield per unit time rather than just the yield or exhaustibility. The distinction is apparently of growing importance as judged by the increasing number of papers these past few years on modelling, optimizing, etc. (McGinnis 1942, 1979; Maurandi and Mantovani 1980, ISSCT Manila 1980; Wright 1972).

It is the intention in this report to review the basic principles of the kinetics of growth of sugar crystals and point out the fundamental approach to optimizing the process, particularly at the crystallizer station where, as it turns out, the benefits are greatest. The chief deterrent to detailed application at this time, as already inferred, is the dearth of appropriate published data. As this becomes available the power of programmed and computerized calculation will provide even more complete and exact solutions to the problem.

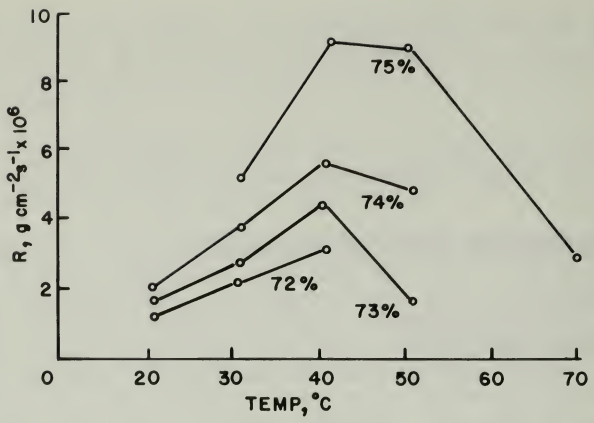

Figure 1.--Crystallization rate for pure sucrose solutions at indicated concentrations, Smythe's data (1971).

GROWTH RATES

The general kinetic characteristic of the total crystallization of sucrose are described by the equation

$$-dc/dt = kA(c-c_s)^n = dW/dt$$

where W will be the amount of sucrose deposited per 100 g of solvent water. n is ideally equal to one but may be greater at low supersaturations and intermediate temperatures (VanHook 1973). For all practical purposes, though, it is customarily assigned a value of unity and its weak dependence on $(c-c_s)$ absorbed in the specific reaction rate constant k. The usual rate value

$$R = \frac{1}{A}\frac{dW}{dt}$$

has units of g $cm^{-2}sec^{-1}$ or equivalent dimensions.

With this understanding, the data of VanHook (1958) are represented as straight lines in Figure 2 in which log-log coordinates are used in order to conveniently include all values from 0° to 80°C. The concentration extends to that point where graining terminates the determination. On this plot are included lines of equal concentration which give exactly the same information as that in Figure 1. The two illustrated demonstrate that the maxima are developed within the working range at low temperatures but not high--being curtailed there by grain formation. A line of constant supersaturation $(c-c_s)$ would be vertical while that at constant relative supersaturation

$$\sigma = \frac{c - c_s}{c_s}$$

would lean just slightly to the right. The first of these simulates behavior in the crystallizer where essentially only deposition of crystals occurs at low temperature while the others may be regarded as more closely related to pan work where feed and water are being manipulated at higher temperatures.

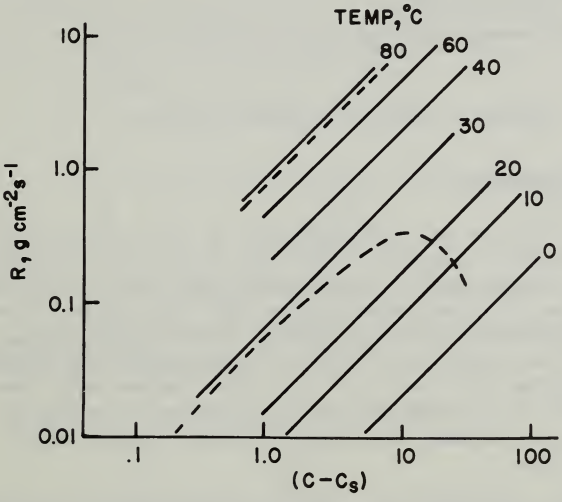

Figure 2.--VanHook's data (1958) for pure solutions.

Three cases must be distinguished in the integration of the above rate equation. Of these, posed in Figure 3, case C is the one considered here as representative of crystallizer work:

$$\ln \frac{c_o - c_s}{c_o - c_s - W} = \ln \frac{\text{total crystallizable}}{\text{uncrystallized}} = k\Delta t$$

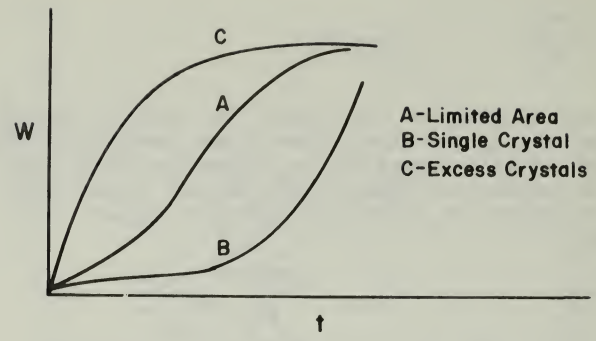

Figure 3.--Crystallization curves.

TEMPERATURE COEFFICIENT

The growth of sucrose crystals proceeds by two consecutive steps of transfer of molecules from the syrup to the growth sites on the surface and actual incorporation there into the crystal lattice. At low temperatures ($0^{o}C$) the second step is much slower than the first and thus dictates the rate. Both increase as temperature rises but unequally; the latter more than doubling with each 10^{o} rise, the former much less. By the time 70^{o} is reached surface integration is much the faster so that it becomes relatively a minor factor in settling the rate.

Now, the series coupling of two first order reactions amounts to an overall reaction rate constant defined as

$$1/k = 1/k_D + 1/k_s \quad (\text{or } W = W_D + W_s \text{ if the resistance}$$

is used) (Schliephake, 1965) where each of the rate constants is temperature dependent according to the Arrhenius equation; namely,

$$\frac{e^{E/RT}}{k_o} = \frac{e^{E/RT}}{k_{o,D}} + \frac{e^{E_s/RT}}{k_{o,S}}$$

Graphically this is represented in Figure 4, in which the respective plateaus correspond to $E_s = 18$ KCal mole^{-1} and $E_D = 5$. The curve is plotted from values at constant $(c-c_s)$ and differs only slightly from that of constant

$$\sigma = \frac{c - c_s}{c_s}$$ by the heat of solution ΔH.

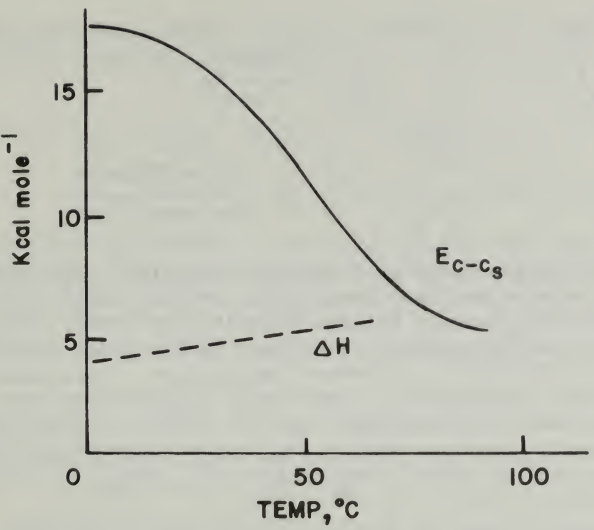

Figure 4.--Activation energies.

The set of growth curves in Figure 2 may now be represented by the analytical expression

$$\frac{1}{A}\frac{dW}{dt} = k_o \; e^{-E/RT} \; (c-c_s) \; e^{-\Delta H/RT}$$

for which E is given by Figure 4. In principle, any unique point, such as the maxima already mentioned or the point of inflection to be described, could be calculated from this equation but it will be found that graphical methods are more useful.

APPLICATION

Crystallizing area generally does not change much in the crystallizer since it is already large to begin with. (Even so, programed computation could readily take care of any change in this respect.) With this understanding, the basic rate equation, at constant temperature, remains

$$1/A \; dW/dt = R = k(c-c_s)$$

Basing all calculations on amounts corresponding to 100 g. water, the time interval for crystallization upon a fixed base area will then be

$$\int_{t=o}^{t-t} dt = -\int_{c_o-c_s}^{c-c_s} \frac{1}{kA} \frac{d(c-c_s)}{(c-c_s)}$$

$$(tA) = \frac{1}{k} \ln \frac{c-c_s}{c_o-c_s} = \frac{1}{k} \ln \frac{\text{crystallizable}}{\text{uncrystallized}}$$

First calculations were performed analytically with the data of Kucharenko as well as those of the writer. These are quite linear for $(c-c_s)$ up to 60 and temperatures 0-90°C. Stirring was gentle. The amounts crystallized from a given syrup initially 250S/100W at different temperature is presented schematically in Figure 5. The figure suggests that this syrup in process of crystallizing, 20° at tA = 10, for instance, will at first give more crystals per unit time by momentarily heating to 30° in spite of lower supersaturation.

The advantage though is lost as crystallization proceeds. Cooling, of course, increases ultimate exhaustion but does not necessarily optimize it. Differences are largely dissipated at higher temperatures where the activation energy of growth and heat of solution become more alike.

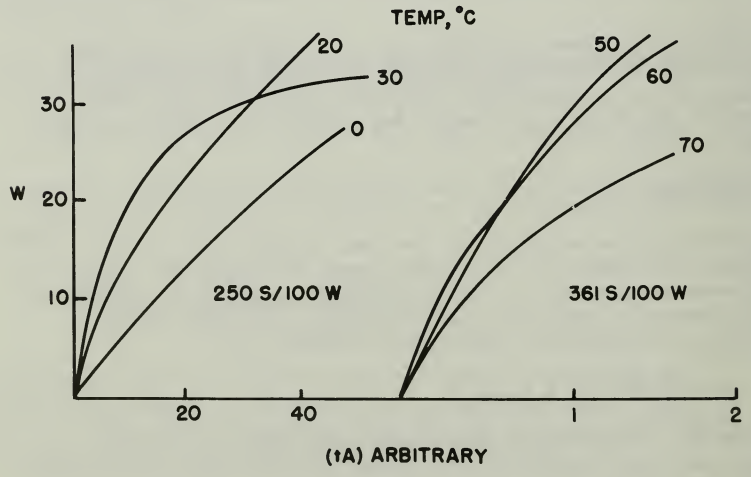

Figure 5.--Weight of sucrose crystallized at low and high temperatures, respectively.

For the non-linear case, the time interval can be evaluated graphically from the area under the

$$\frac{1}{R} \text{ vs } (c-c_s) \text{ plot: } (tA) = \int_{c_o-c_s}^{c-c_s} \frac{1}{R}\, d(c-c_s)$$

This was done with Smythe's data and exactly the same pattern was realized. They are, therefore, not given here but rather the calculations will be illustrated with real juices, for which the only suitable data available to the writer are those of McGinnis (1942, 1976) and, more recently, of Mantovani(1980).

The former seems suited in the sense of displaying activation energies which increase with falling temperature but only at relatively low supersaturations. Above $\sigma = 1.5$ false grain and viscosity render the calculations futile. A plot of I/R against C out to $\sigma = 0.5$ gave a family of point-to-point curves which converged at high C's and diverged at low, but with some cross over in between. This is illustrated in the following sketch in which only a few of these unusual curves are given in order not to obliterate the patterns with the complete manifold.

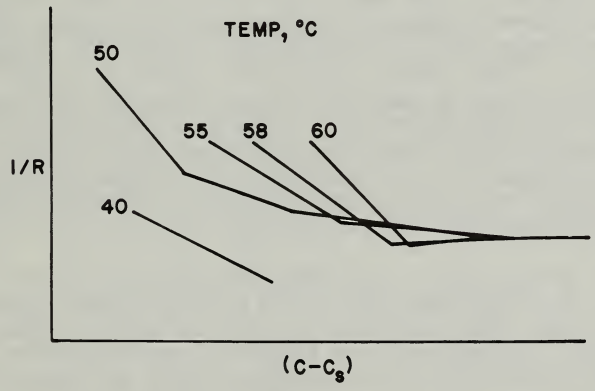

Figure 6.

Accordingly, the W-t pattern for a solution containing 350 S/100 W was constructed from the areas under these curves in this critical region and the result given in the following figure.

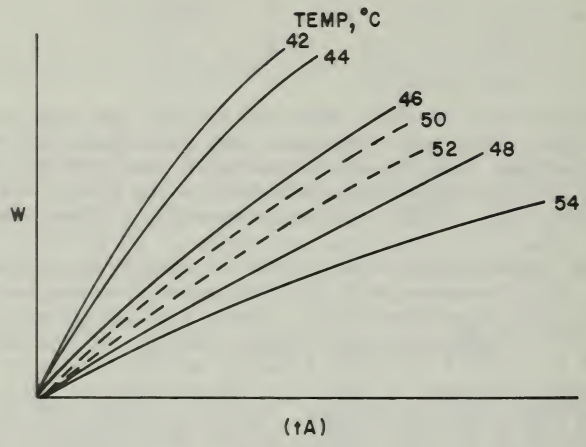

Figure 7.

The time required to crystallize a definite quantity of sucrose at first increases as the temperature rises but then recedes for a space (50-52°) before climbing again--reflecting the interplay of temperature on crystallization rate and solubility.

The same pattern can be perceived in part in the recent data of Maurandi and Mantovani (1980). Here again the calculation is curtailed on account of presumably false grain and viscosity causing maxima at high supersaturation. Below this point the following W-t plots have been constructed from the areas under the corresponding 1/R - C curves.

Here again we can surmise that temporary heating of say a massecuite partly crystallized at 40° will yield additional crystals quicker than otherwise but only for a time. Soon the greater yield accruing from the lower solubility at 40° exceeds the accelerated crystallization at 60° but with a higher solubility. Such temporary heating could also be interpreted as an endorsement of the advantage of heating over dilution before purging (Moritsugu, 1974).

It must be recognized throughout that these speculations are unrealistic in that they assume instantaneous temperature adjustments. With programmed computations it will be possible to modify them for varying cooling rates and to properly assess the role of the critical optimum crystallization (McGinnis, 1942), the limitations due to false grain formation

(Schliephake, 1966), fast vs. slow cooling in the crystallizer (Meade-Chen, 1977), the possibility that established practises may not be optimal (Frew and Wright, 1974), etc. To the above there is an analogous situation in the pan, where growth rate is pitted against evaporation rate (Bosworth, 1959).

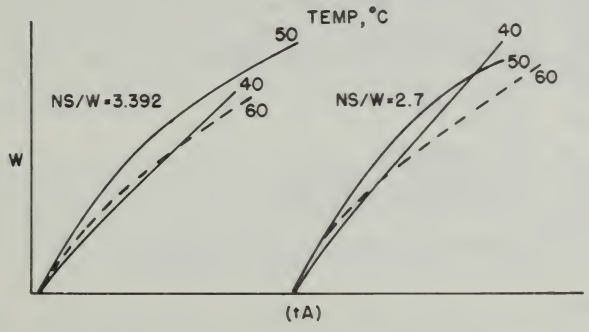

Figure 8.

The main thrust of these highly theoretical speculations is to suggest that careful consideration of the temperature coefficients of growth (activation energy) may be helpful in understanding and maybe even improving operation at the crystallizer station. This is by no means a new concept; R. E. Lionet and P. W. Rein at the recent Manila meeting of ISSCT being very specific on this point. The graphical method may be one means of circumventing the non-linear nature of the crystallization process and its unusual temperature behavior. Several other papers and discussions on modelling and optimizing at this same meeting, as well as some recent abstracts on the benefits of cycling temperature (C. A. 84(4) 19509(1976); 92(8)6062(1980); 92(12)92911(1980) have served to prompt the writer's thoughts in this direction. Hopefully, his analysis may stimulate and be of some use for further investigations in this field.

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DISCUSSION

M. MATIC: This is a question that I have asked in the past, and I wonder if I will get an answer now. It is quite possible to understand how raffinose could be incorporated into the sucrose crystal because raffinose is not that different from sucrose in shape and size. Do you have an explanation for this process of incorporation in the case of dextran where the molecules are enormous in comparison to sucrose, and for why only specific dextrans are involved?

A. VANHOOK: There are two factors involved; the chemical factor or similarity and also the structural or crystallographic factor. Chemically there is no dispute. Sucrose is a glucofructoside, raffinose is a galactosucrose, dextran is a polymer of glucose. So, the chemical requirements are there. Now, when you come to the crystallography they are not. Dextran isn't even crystalline. It's a high polymer and there is no crystallinity to it, as far as I know. Raffinose is crystalline but it is in a different crystal system from sucrose. Raffinose is orthorhombic while sucrose is monoclinic. So, the structural features are absent in both cases. That is why you don't have a strong epitactial union between the two sugars. If you look at the structure of the sucrose crystal and then at the structure of the raffinose crystal, you will find that while the overall dimensions are incompatible, there are certain orientations of the two that are compatible. Similarly for glucose: glucose will latch right onto the a-face of the sucrose crystal even though the overall dimensions are not the same. There is an orientational factor that is compatible. Therefore, while there may not be a strict stoichiometry between sucrose and raffinose (none of these

things are known to form any kind of complex with sucrose) there is certainly strong chemisorption. Detailed X-ray work shows absolutely no distortion of the sucrose lattice when raffinose is incorporated into the crystal. And neither is there any change in the sucrose lattice when dextran is adsorbed on the sucrose. But nevertheless it is there, and throughout the crystal. So, the conclusion that I have come to is that it is present there either as a solid-solid solution or as an intercalcate compound. In intercalcate compounds one molecule slips in between the layers of another one. If you look at sucrose, as you very well know, along that 100 plane which is the cleavage plane there is plenty of room for other molecules to fit in. That is the way I see the situation today--it may answer your question.

M. CHO (Audubon Sugar Inst.): In your analytical expressions of the crystallization, what bothers us from the engineering point of view is that you seem to be missing a diffusional term or what we might call the convective mass transfer effect. Inclusion of this term would really change the constant.

A. VANHOOK: The constant of which I was talking is composed of a diffusion-transport factor, this convective constant that you are talking about, plus a surface integration or geometric factor. My constant is the composite of both.

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_S}$$

If you look at the crystallization of sugar you find that at high temperatures, from 50°C up, the diffusiove or convective or transport constant is the rate controlling one. It is the slower of the two. At low temperature the surface integration one is the more important, the rate controlling factor of the two. Both factors are in the constant and can be analysed in terms of their Arrhenius activation energy parameters.

M. CHO: You defined stirring as gentle. How do you define gentle quantitatively?

A. VANHOOK: By gentle stirring I mean slow tumbling, in my own work with the buoyancy method, I had a ring surrounding the crystal that moved up and down slowly in a reciprocating way. This is to distinguish it from the way Max Smythe determines his growth rate in which he uses a propeller-like stirrer at about 3000 RPM so that he has a very high Reynolds Number.

Panel discussion on dextrans

INTRODUCTORY REMARKS

Margaret A. Clarke

Cane Sugar Refining Research Project, Inc.

Dextran is a word we have all been hearing a great deal lately. The dextran problem has always been with us: with refiners, with sugar producers and with cane growers. We have heard tales of different aspects; we have heard of raw sugar factories having to close down because of slime formation, and about needle grain sugar in refineries that blocks up centrifuges and makes it an impossibility to put five pounds of sugar in a five-pound bag. We have heard that dextran is associated with mechanical harvesting, although it can be found with hand cut cane too. About three years ago, the industry started to hear a good deal more frequently about dextran. There were two reasons for this: two sets of events happened to occur at the same time that brought this problem to the attention of sugar refiners, certainly all those in North America.

The first of these reasons was that a series of cargoes of rather poor quality off-shore raw sugars was arriving. These raws were such that a great deal of sugar - much more than normal - was sent to recovery. Remelt houses had increasingly higher loads. This happened just at the time that fuel prices started to escalate. Everyone noticed the increased remelt load rather more sharply than they would had the fuel prices not changed, and everyone began to question the reasons for increased loss to recovery with these sugars. At that time, the Cane Sugar Refining Research Project started some investigations on dextran, in light of the current problems. Lots of people, of course, have worked on dextran in its different aspects, particularly the research organizations in Australia and South Africa. Emory Coll and Earl Roberts of CSRRPI began to look at where dextran was coming from and what we could do about it. Several sugar refining and sugar milling companies have been working with us on this problem; we are glad for this sort of cooperation.

There are some basic questions about dextran that our panel is going to consider this afternoon. Each panelist has a

different area of expertise. The questions that we want to consider boil down to: where, what, when, who, and how? The first question is "where" does dextran come from? One answer we frequently hear is that: Dextran is a field problem. Dr. Irvine is going to talk about the field problem and about the "where" of the dextran question.

"What" is dextran exactly? We know that it is not a single compound. We use the term "dextran" very generally to describe a lot of compounds that behave in certain ways in process. Dr. Matic is going to explore this area: What is dextran? He is going to tell us something about the behavior of dextran in raw sugar mills. That's the other answer to the "where" question: - It's still a mill problem.

"When" is the refiners' problem because when we get dextran into a refinery, we usually get it going right out again into the refined sugar, as Dr. C. C. Chou of Amstar has shown in his work on behavior of dextran in various refining processes. Richard Priester is going to discuss his company's refining experience with dextran.

"Who is concerned about dextran?" may seem to be stretching this analogy a bit, but who among our customers can we expect to have problems related to dextran in the sugar? Dr. Graham Vane has prepared a discussion on some of these customer problems.

The last question, "How?" relates to everyone of these problem areas. How do we know if dextran is present, and if it is, how much is present? How do we know how much trouble to expect in process? Earl Roberts is going to tell us the current state of the art in dextran analysis, and talk about some of the problems with currently available methods.

Panel discussion on dextrans

FIELD ORIGINS OF DEXTRAN AND OTHER SUBSTANCES AFFECTING SUCROSE CRYSTALLIZATION

James E. Irvine

U.S. Sugarcane Field Laboratory

A number of substances have been implicated in problems associated with sucrose crystallization. Although dextran has achieved the greatest notoriety in recent years, inorganic ions (especially potassium) and polysaccharides other than dextran may affect sucrose solubility, the rate of crystallization, and the shape and purity of the crystals.

Sugar recovery has greatly improved during the last two centuries. When open kettle sugar was commonplace, about 200 gallons of molasses were produced for every ton of sugar. With recovery improved by the vacuum pan and efficient centrifuges, only 75 gal/ton are produced in good years, although the number is higher when field conditions retard crystallization. Sugar recovery has continued to rise since the advent of the modern factory, and this has been brought about by the sugarcane breeders (in Louisiana, Argentina, and, recently, in Hawaii) who have put more sugar into new varieties with higher purity.

In spite of the successful efforts of the factory engineers and the breeders, crystallization problems continue. Many of these can be traced to the worldwide increase in mechanized harvesting. In much of the sugarcane world, fresh, hand-cut, hand-cleaned sugarcane is no longer available, and factory managers who disdained trash levels above 3% now routinely accept 10% that includes a generous dose of salts from the accompanying field soil.

Field soil is gathered by the grab loader, the chopper harvester, the push-rake, and the Hawaiian drag-line harvester. Besides the problems with wear and clarification, soil frequently contains high quantities of potassium; potassium increases sucrose solubility and lowers its recovery, creating more molasses. The cane plant itself is an injudicious consumer of potassium, greedily accumulating it. Potassium

concentration in sugarcane forms a gradient increasing from the bottom upward, so the tops are far richer than the stalks; perhaps this is one of the several reasons why factories reject green tops.

Besides having no sucrose, green tops are rejected for the high starch content of the cane leaves, particularly at the day's end. Starch also occurs in the intercalary meristem of the stalk; it serves as an energy source for meristematic growth that turns up the tops of lodged stalks. Varieties differ in starch content; the difference is more pronounced in the stalks than in the tops. There is some evidence that high sucrose varieties are high starch varieties. The problems associated with starch and crystallization can be minimized through variety selection and by employing harvesters which exclude green leaves.

Starch, a storage polysaccharide, is usually negligible in concentration in properly cleaned cane. Similarly, gums, a group of structural polysaccharides, may also be minimal in concentration by proper cleaning and topping. Gums, a generic term to include pentosans, pento-hexosans, hemicellulose and pectins, are substances intimately involved in the formation of the plant cell wall. Modern physiology suggests that molecules of the dominant structural polysaccharide, cellulose, are held together by hydrogen bonding, and that groups of about 40 molecules form cellulose fibers which are held together by a complex of pento-hexosans and hemicellulose. In young tissue, the non-cellulose polysaccharides form 70% of the dry weight of wall material; in mature tissue, they account for only 10 to 20%. In addition to their presence in the immature stalk and leaf tissue of cane tops, gums may also be present as deterioration products in dead leaves. Preliminary analyses by Roberts (unpublished) showed a sugar-free extract of dead leaves capable of producing pentoses and hexoses on hydrolysis.

Workers in Australia and South Africa detected a new polysaccharide, an alpha-glucan, from cane neither burned nor frozen, but stored a while before milling. It was named sarkaran in South Africa, and it is thought to be a product of naturally occurring enzymes rather than microbial degredation.

Two other polysaccharides, however, are metabolic products of bacterial growth. Levan, the fructose polymer produced by Bacillus subtilis and B. cereus, is of factory rather than field origin. Dextran, the glucose polymer produced by Leuconostoc mesenteroides is of both field and factory origin. Mentioned by Browne in 1912 as a sugarhouse problem, dextran was recognized in cane in the field by Owen, who realized the role of Leuconostoc in frozen cane in Louisiana. Egan called the effects of Leuconostoc infection sour storage

rot, and he considered it a disease of post-harvest sugarcane (see below). Leuconostoc can invade sugarcane storage tissue before harvest. Tests with the variety L 62-96 under irrigated culture in Morocco suggested that Leuconostoc entered the pronounced growth cracks of this variety at levels detectable by the haze analysis of Nicholson and Horseley (undamaged standing cane is free of internal contamination with Leuconostoc).

Burning standing cane to facilitate harvest, happily enough, reduces trash and its undesirable components and, unhappily, removes the protective surface wax causing cracks in the rind and cooking the underlying storage tissue. With really good burns, the structural integrity of the stalks is so weakened that the crop sags and collapses, and juice begins to ooze from the damaged stalk; the juice provides a feast for Leuconostoc.

At the other end of the temperature scale, the freezing of cane stalks produces similar results. Mild freezes kill the leaves and the terminal bud, and other than stopping photosynthetic sucrose accumulation, these freezes have little effect on sugar recovery. Moderate freezes kill the lateral buds and the upper internodes and Leuconostoc then enters, perhaps through the dead buds. After a moderate freeze, souring begins in the upper internodes, but lower topping of the stalk at harvest easily solves that problem. Severe freezes may kill all of the aboveground tissue, and freeze cracks open in the stalk and permit the ready entry of Leuconostoc. After a severe freeze, souring and dextran formation follow rapidly, and processing may be impossible in 10 to 20 days, depending on the post-freeze temperatures.

The United States is unique in its penalty system for the purchase of frozen cane. Contracts stipulate that deductions based on titratable acidity can be implemented when difficulties occur in the sugarhouse following a freeze. The penalty serves to encourage the farmer to top low at harvest and get his cane delivered as rapidly as possible after cutting. The penalty is based on the increase of lactic and acetic acids following freezing, but it does not differentiate between spoiled cane and cane naturally high in organic acids due to variety or soil type. Nor does the penalty recognize the real culprit, dextran. The sugar industry, although it is aware that dextran is the cause of freeze-associated problems, lacks a method of measuring how much dextran is in the farmer's cane. Following the last freeze that affected the Louisiana sugarbelt, we sampled massequites in a number of mills located on a north-south axis. The northernmost mills were unable to crystallize, the central mills were having needle-grain and retention problems, and the southern mills had no problems and fine crystals. The

level of dextran in the massequites was closely associated with the elongation of the crystals.

Sugarcane deterioration whether in sound, burned, or frozen cane, can be accelerated by the bruising, tearing and slicing engendered by harvesting. Sound, whole-stalk cane seldom shows elevated dextran content; burned or frozen whole-stalk cane will deteriorate more rapidly with the superimposed mechanical damage of knives, sticker chains, chain slings, and mechanical grabs. Hot weather and abundant inoculum can cause overnight loss of cane that has suffered these tortures.

If refineries have experienced an increase in the occurrence of dextran in raw sugars, part of the reason might be the increased popularity of the chopper harvester. Designed to fill the gap between the high-tonnage Vee-cutter and the light-tonnage soldier harvester, the chopper harvester pushes cane over, cuts it at the base, pulls it in, and chops it up. The billets so formed are of varying lengths; they are carried up an elevator past one or two trash extractors and dropped into an accompanying wagon. The chopper-harvester is most effective when the cane to be harvested has been burned, and there is less material to impede the progress of the machine. The cane is cut into billets to facilitate trash removal and to promote high load densities.

When the chopper-harvester first replaced hand-cutters in Australia, it had been common practice to store cane over the week-end break so that the mills could begin crushing without delay on Monday morning. In 1962, the Mulgrave mill, in tropical North Queensland, complained of serious problems with Monday cane. Investigations by Egan, of the Bureau of Sugar Experiment Stations, showed the population of Leuconostoc to be building up rapidly in the chopped and burned cane, producing unmanageably high levels of dextran. Egan showed that each cut made by base-cutters or chopper knives inoculated the stalk piece, and that dextran could be detected in less than 24 hours after inoculation. He showed that mists or dips applied to the billets immediately after cutting were ineffective in preventing what he called sour-storage rot. Egan found that the two practical measures to diminish the dextran levels in harvested cane were to prevent splitting and fraying through the use of sharp knives and to insure rapid transport and processing of chopped cane.

In established sugarcane areas, Leuconostoc is present the year around. Varieties do differ in their response to the organism; although the differences may be of statistical significance, they are of no pragmatic significance.

Breeders and pathologists are unlikely to provide a cure for sour-storage rot and the accompanying production of dextran. The solutions available are those suggested by Egan as implemented by managers having to use chopper harvesters. Careful attention to equipment maintenance and to rapid cane transport and handling minimizes the problem. The real solution would be a harvester which combines the tonnage capacity of the chopper harvester (without chopping) with the flexibility of the soldier harvester and the economy of the Vee cutter.

Panel discussion on dextrans

DEXTRAN PROBLEMS

Milo Matic

Audubon Sugar Institute

Occurance of needle grain, usually in low grade massecuites, is not a new phenomenon but its importance in cane sugar industry increased dramatically with the advent of chopper harvesters. Use of these machines may lead to fast deterioration of harvested cane through infection with bacteria of Leuconostoc species which produce dextran, a substance which plays a role in crystal elongation. In the past this was mainly a problem concerning raw sugar producers but refining industry is also becoming aware of it. One can expect therefore that before long a new sugar quality parameter will be introduced which would measure the propensity of raw sugar to produce elongated crystals on refining. It is of considerable importance therefore for both the raw sugar producers and the sugar refiners that the adopted test be specific and its results meaningful. Unfortunately, the haze method for determination of dextran, tentatively adopted by ICUMSA falls short of these requirements and its indiscriminate use may lead to a lot of confusion.

Out of the multitude of dextrans (α-polyglucans having more than 60% 1,6 linkages) only the one produced by bacteria of Leuconostoc species has been shown to cause crystal elongation and is therefore of special importance in sugar manufacture. This particular dextran has high molecular weight and very little branching (about 90% 1,6 linkages). Quantitative determination of this polyglucan requires complicated procedure and the haze method was developed in order to simplify the analysis. When Leuconostoc contaminated samples are analyzed, satisfactory results are obtained by this method. However, the haze method is not specific, since other polysaccharides insoluble in 50% aqueous alcohol will be recorded as dextran when analyzed by this method. For example, a number of indigenous cane polysaccharides which constitute the so called gums fraction of raw sugar will react in this way. Yet none has been

shown t‹ cause crystal elongations. Another example is sarkaran an α-polyglucan found in stale, whole-stalk harvested cane. This polysaccharide has only about 25% 1,6 linkages and does not produce elongated crystals. If present in raw sugar however, it will be recorded as dextran by haze analysis. Thus misleading information will be obtained when haze analysis is applied to raw sugars uncontaminatd by Leuconostoc dextran.

To complicate the issue even further, it is known that addition of dextran to pure sucrose solution produces only a limited degree of crystal elongation. To obtain extreme elongation found in sugar factory products, either another impurity or some change in physical conditions of the sucrose solution appears to be required. South African experience with crystal elongation indicates that substances other than dextran may be involved. For example, very poor correlation (corr. coef. 0.36) was obtained between dextran, as analyzed by haze method, and either degree or percent of crystal elongation found in about forty massecuites. Kestose, a trisacharride present in cane and known to modity crystal habit of sucrose was suspected but here again the degree of elongation obtained when sucrose crystal was grown in presence of kestose isomers was too small to explain the needle grain found in low grade boilings.

Clearly, there is still a lot more to be done before a satisfactory answer to crystal elongation is found. In the meantime a more specific method for determination of dextran produced by Leuconostoc species would help in eliminating confusion.

Panel discussion on dextrans

DEXTRANS IN RAW SUGAR

Richard Priester

Savannah Sugar Refinery

Raw sugar quality is one of our most important concerns. When quality is poor, we see significant decreases in our melts, which in turn drives upward our per unit costs.

One of the most serious deficiencies related to raw sugar quality directly affecting production is poor filterability. When we have experienced such problems, we have noted in most instances that the raw sugar we were melting contained large quantities of insoluble material. For years we could know consistently that if we were experiencing flow reductions in liquor through our Sweetland Presses, the raw sugar input was, no doubt, high in particulate matter.

However, in recent years, even though the primary offender in regards to restricted flows has still been high quantities of insoluble matter in our raws, we have seen an increasing number of instances where flow problems would occur when the amount of sediment in the melt was normal. This, of course, led to further investigations.

In one instance where we were experiencing such a problem, we were melting raw sugar from only one source. We contacted the supplier, and found that they were experiencing similar problems in their mill. They had determined that during this period the dextran content of the cane juice, and hence, the raw sugar being produced was running abnormally high. After this initial discussion on the subject, we made a point to keep close contact with this mill regarding the problem. There were further instances where filterability decreased when processing raws from this source, and it was learned that the problem again related to dextran content in the raw sugar. The supplier reported that since they had started using mechanical harvesters, they had seen this problem more frequently. They further said that during occasions when heavy rains forced them to leave cane stalks in the fields for a delayed period of time

before sending them to the mill, this problem became more evident. Since the harvesters cut the cane stalks in numbers of pieces, the microorganisms that cause the dextrans to form, have more surface (i.e. on each end of the stalks) to attack.

It was observed that during periods of time when the dextrans were in excess in the raw sugar being processed, the presence of elongated grain began to be noticed in the low purity boilings in our plant. This, of course, is another undesirable byproduct of this problem.

During this past year, The Cane Sugar Refining Research Project in New Orleans, Louisiana, has made efforts to develop a quick reliable method for the determination of dextrans. This is certainly needed, as much more should be known about this problem. Our company has not had the need in past years to explore this subject. However, since we have been introduced to the problem more frequently through recent experience, we will be looking into this matter further.

Panel discussion on dextrans

PROBLEMS ARISING FROM THE PRESENCE OF DEXTRAN IN SUGAR PRODUCTS

Graham W. Vane

Tate and Lyle Limited

Whilst dextran in sugar products is of considerable concern to the manufacturers--if only for the added processing problems and the "lost" sucrose--not much attention has been paid to the problems which the consumer buys along with the sucrose. It is perhaps timely for us to consider this very important aspect, which is largely confined to sugar products of cane origin.

Crystallisation seems relatively ineffective at lowering the dextran level in crystalline products which means that dextran can occur at significant levels in both liquid and granulated products. We have heard from Dr. Chou of the limited ability of current refining processes to remove dextran from sugar liquors. I would like to enlarge on this point. I have in recent years made some study of the lowering of dextran levels in refinery processes and have concluded that our refining processes (affination, phosphatation, carbonation, char, granular carbon, ion exchange resins and crystallisation) are not effective in removing this troublesome impurity. Only processes where a fine filtration step is involved seem to have any significant effect; thus of the preceding group, only carbonation has some limited effect, depending upon the size and shape of the chalk particles. I would say that it depends to a large extent on exactly how the unit processes are conducted and also, of course, on the methods used to measure the dextran level. Whilst we have used alcohol haze to some extend, we have also used more specific analytical methods, such as alcohol haze before and after dextranase treatment.

Coupled with the increasing use of mechanical harvesting, the foregoing indicates that dextran levels in sugar

products should have increased in recent years. It has certainly been our experience that this is so; until recently the lack of reliable analytical methods for detecting and measuring dextran has undoubtedly meant that some problems due to dextran have not been so ascribed. In the recent past we have measured dextran levels in a range of sugar products and have observed a significant increase and, in general, the problem appears to originate in the raw sugar. I am not aware, however, of a significant increase in customer complaints in recent years, suggesting that dextran at the levels commonly encountered in sugar products does not cause great problems. Our measurements have indicated that granulated product contains 0-100 ppm, perhaps double this in non-crystalline material, and sometimes several thousand ppm in molasses. Raw sugars vary from 100 to 1000 ppm or more, and at least in refineries that I have worked with, "high in equals high out" is the result. Thus we have encountered refined products with as much as 500 ppm present, though I hasten to add, not from our refineries.

The most obvious problem that consumers encounter is that of alcohol haze. This may of course be due to other impurities but the refinery operation is more efficient in the removal of the latter than dextran. There does not appear to be any significant problem with alcoholic liquor manufacture in Europe at present, though I have heard of some such problems in the U.S.A. which are said to have increased in recent years. These problems have certainly been ascribed to dextran and probably rightly so. A problem that has arisen in Europe and ascribed with certainty to dextran, is fever reactions in hospitalised patients infused with dextran-containing invert sugar solutions. The incidence is low (1 in 30,000) and relatively mild but is of course potentially dangerous to already unfit people.

A most interesting example of a consumer problem is the distortion of hard candy. Traces of dextran in the sucrose used retards the setting of the candy pieces, and distortion can result causing problems, particularly at the packaging stage. The level of dextran required to cause a problem is a function of molecular weight, the recipe used for the candy mix and the nature of the processing equipment. I have recently made a special study of this problem and intend to publish the results in the near future, and so will not elaborate further at this time.

Recently, we learned of a problem with a tabletting sugar, which may have been due to the presence of dextran. Certainly the sugar used had a high alcohol haze, and the tablets produced were very prone to capping (that is, they tended to fracture across their long axes). It is not clear

to me how dextran could cause this problem, or for that matter cause hard candy to distort. In the latter case, it could be affecting micro-crystallisation of sucrose thereby affecting the rheology of the candy piece but this was not proven.

Finally, while not necessarily a consumer problem, it seems that dextran can have adverse effects on sucrose transformation. We have not proved conclusively that a correlation exists here, but it would be expected that dextran would impede the crystallisation process in this case. We do have some evidence for this, having successfully transformed an 80 purity liquor but failing to transform 90 purity raw syrup; the dextran levels were 200 ppm and 1000 ppm respectively. However in small scale experiments the effect was not demonstrable for high purity systems whereas dextran (MW 150,000) was shown to have an adverse effect when added to a well defecated 90 purity system. The difficulty that we encountered here was to meaningfully scale down the transformation system, and this may have influenced the results.

So it appears, fortunately, that our customers do not in general regard dextran in such unfavourable light as ourselves. It is possible that with increased awareness we are now seeing the highest levels of dextran in our materials. We look to the raw sugar manufacturers to alleviate the problem, rather than looking for measures to remove dextran at the refinery stage.

Panel discussion on dextrans

DEXTRAN ANALYSIS: METHODS AND PROBLEMS

Earl J. Roberts

Cane Sugar Refining Research Project Inc.

Dextrans are essentially straight chain polymers of α(1-6) linked glucose units with some α(1-4) and α(1-3) branches. These polymers are formed by the action of Leuconostoc mesenteroides on sucrose. Other glucose polymers produced by soil borne organisms are scleroglucan, pullulan, sarkaran, and curdlan. The molecular weight of these polysaccharides may exceed ten million.

All of these glucans create slimes and dramatically increase solution viscosity. Stale cane and certain problems in harvesting cause an increase in dextran content in raw sugar. This has become a major problem for cane sugar refiners. For this reason a rapid specific and accurate method for the determination of dextran is needed for both raw sugars and cane juice. To our knowledge only three methods for dextran have been published, neither of which is specific for dextran, and two methods for total polysaccharides. The methods are as follows:

1. CSR Method for the Determination of Dextran in Raw Sugar (Meade and Chen 1977a).

The above CSR method is non-specific for dextran but this is not a real problem for the refiner because in the refinery any polysaccharide that interferes with the process acts like dextran, and is classified by the general term "dextran."

Dextran and other polysaccharides produced by soil borne organisms are probably present in a wide range of molecular weights ranging from a few hundred to several million. For this reason 50% alcohol, as used in the above method, probably does not precipitate all of the lower molecular weight polymers. In addition some of the dextran is of sufficiently high molecular weight that it is insoluble. In this procedure the solution being tested is filtered with filter aid before the alcohol is added; consequently, the high molecular weight material is lost. The high molecular

weight insoluble dextran is the major cause of unusual turbidity in refined sugar from high dextran raw.

2. Analysis of Dextran in Sugar--an Enzyme Method (Richards and Stokie 1974).

This method is probably the most nearly specific method. However, the dextranase would have to be completely free of other polysaccharide splitting enzymes such as amylase to prevent starch from interfering. Such a purified enzyme is not readily available. In addition, dextranase is specific for α(1-6)linkages and will not break other linkages. Since dextran has α(1-3) and α(1-4) linkages, the dextranase should break the dextran molecule up to some extent, but will not break it down to individual glucose units. Many of the fragments formed may be too large to pass through the pores of the dialysis tubing. This method is also much too long and time consuming to be used as a factory control method for raw sugar or cane juice.

3. An Enzyme Technique for the Detection of Dextran in Cane Juice and Prediction of Viscosity Increases (Geronimos and Greenfield 1978).

This method is designed primarily for the detection of the presence of dextran in cane sugar products. It is based upon the measurement of the viscosity of the solution before and after treatment with the enzyme dextranase. In this procedure the molecular weight must be known for the method to be quantitative. Therefore, the method is not suitable for factory control analysis.

4. Thin Layer Method for Dextran Determination (Meade and Chen 1977b).

This method gives a crude estimate of the total polysaccharides and is not recommended as a factory control method.

CSRRPI METHOD

ESTIMATION OF THE SOLUBLE POLYSACCHARIDES IN SUGAR -

A rapid test for total polysaccharides

INTRODUCTION

This procedure determines total soluble polysaccharides: dextran, starch, mannans, ISP (arabinogalactans) and any other soluble polysaccharides in sugar. The soluble polysaccharides are those of special concern to the refiner because they remain in solution throughout processing.

This procedure is based upon the precipitation of the polysaccharides from a sugar solution by alcohol. The precipitated polysaccharides are filtered off and the filter is washed with 80% V/V alcohol until free of sugar. The polysaccharides are dissolved out of the filter by boiling in 1% V/V sulfuric acid. The polysaccharide solution thus obtained is adjusted to a definite volume, filtered, and the mg of polysaccharides per ml of solution is determined colorimetrically.

APPARATUS AND MATERIALS

Apparatus

Millipore filter - 300 ml millipore filter holder with fritted glass bottom.
Millipore filter - Type LS Teflon filter paper, 47 mm in diameter and pore size of 5 microns.
Filter aid - Celite analytical filter aid
Volumetric flask - several volumetric flasks of 200 ml and 250 ml.
Flasks - Several 250 ml Erlenmeyer flasks.
Funnels - Several short stem funnels 70 mm in diameter.
Filter paper - Whatman No. 42 ashless filter paper 12.5 cm diameter.

Solutions

1% V/V sulfuric acid - dissolve 5 ml of concentrated sulfuric in 495 ml of deionized water.
5% W/V phenol solution - place 5 g of phenol in a 100 ml flask and add deionized water to the mark, and shake until dissolved.
80% V/V alcohol - measure 400 ml of absolute ethanol in a 500 ml flask, add 100 ml of water and stir.
Alcohol - absolute ethanol
Concentrated sulfuric acid.

Preparation of polysaccharides: Dissolve 100 g of the sugar to be analyzed in 150 ml of deionized water and adjust the volume to 250 ml in a volumetric flask and let stand undisturbed for 30 min.

Precipitation of polysaccharides: Withdraw 10 ml of the sugar from the center of the flask with a pipet and place in a 100 ml beaker, add 0.5 g of celite analytical filter aid, stir, and add 40 ml of absolute ethanol. Filter the solution with suction on a Millipore filter using a type LS Teflon filter paper, 47 mm in diameter, and pore size of 5 microns. When the liquid has disappeared from the surface of the filter aid the filter is washed with 150 ml of 80% V/V alcohol to remove sugars. This is conveniently done with the 80% alcohol contained in a plastic wash bottle. The 80% alcohol should be carefully applied down the inside walls of the funnel in 20-25 ml portions, allowing each portion to disappear from the surface of the filter aid before adding the next.

Elution of polysaccharides: Quantitatively transfer the filter aid and filter paper to a 400 ml beaker and add 150 ml of 1% V/V sulfuric acid solution. Boil the mixture for 5 minutes. Remove the filter paper and rinse with water, allowing the rinse water to go into the beaker. Quantitatively transfer the contents of the beaker to a 200 ml flask, cool to room temperature and dilute to the mark with deionized water. The volume of the filter aid is insignificant. Filter the solution through a Whatman No. 42 filter paper by gravity, discarding the first 10-15 ml of filtrate. The next 10-15 ml may be used for the determination. It is not necessary to filter the entire solution.

Development of Color: Pipet a 2 ml aliquot of the polysaccharide solution into a 20 mm x 150 mm test tube and add 1 ml of a 5% aqueous solution of phenol. Ten (10) ml of concentrated sulfuric acid is then added at one time from a pipet with a large opening. After the solution has cooled to room temperature (about 30 min) the color is read on a spectrophotometer at 485 nm against a blank prepared in the same way as the sample except that 2 ml of water is used instead of the polysaccharide solution. The color determinations and blanks should be done in duplicate. If the percent transmission in the duplicates varies more than 2%, both should be repeated. The mg of glucose per ml of solution corresponding to the color reading is then determined from the standard curve. Take 90% of the glucose value to convert it to polysaccharide value.

Preparation of Standard Curve: Place 100 mg of pure glucose in a 1000 ml volumetric flask and make up to the mark with

deionized water. For each point on the curve dilute this stock solution as follows:

ml stock solution	dilute to	mg glucose/ml
10	100 ml	0.01
20	100 ml	0.02
30	100 ml	0.03
40	100 ml	0.04
50	100 ml	0.05
60	100 ml	0.06
70	100 ml	0.07
80	100 ml	0.08
90	100 ml	0.09
100	---	0.10

Place 2 ml of each solution in a 20 mm x 150 mm test tube, and add 1 ml of a 5% aqueous phenol solution to each tube. Then 10 ml of concentrated sulfuric acid is added all at once from a pipet with a large opening. When the solutions have cooled to room temperature the color is read on a spectrophotometer at 485 nm against a blank prepared in the same mannner except that 2 ml of water is used instead of the glucose solution. The color readings are then plotted on graph paper. If the color is read as percent transmission it must be plotted on semi-log paper of one cycle. If the color is read as optical density the values are plotted on square paper. The curve is used to determine the polysaccharides corresponding to the color measurement in an unknown solution.

INTERFERENCES AND SOURCES OF ERROR

The phenol sulfuric acid reaction is extremely sensitive to all carbohydrate material including cellulose and starch. Every precaution must be taken to make sure that all glass apparatus is free from dust particles, pieces of tissue, etc. which may render the results erroneous. All glassware should be washed with deionized water immediately before use. The 5% phenol solution should be prepared fresh about every ten days. It is important that every detail of the procedure be followed, including use of the specified filter paper.

The teflon Millipore filters may be reused a number of times, until they become plugged or develop a hole.

In this method the polysaccharides are precipitated by making the solution 80% V/V with alcohol. This precipitates almost all of the polysaccharides which are filtered off, and washed free of sugar; the precipitated polysaccharides are partially hydrolyzed before the color forming reagents are added. In this way the high molecular weight polysaccharides are

included. The phenol-sulfuric acid color reaction has been well established as a reliable method for carbohydrates.

The method is simple to perform and is rapid. It should be well suited for factory control work.

Possible problems lie in non-specific order of precipitation of the various polysaccharides, and the necessity for precise and reproducible performance of the procedure.

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Panel discussion on dextrans

OPEN DISCUSSION

J. C. P. CHEN (Olin): We have heard about dextran in refined sugar and traced it back to dextran in raw sugar, and then traced it back to dextran in the field. I feel that we must answer; how to prevent dextran? and how to cure dextran? Dr. Irvine talked about things to avoid in harvesting to prevent the formation of dextran. It appears that the cure is more difficult.

The method of analysis is still not satisfactory because all do not agree on the standard. Hawaii is using 70 000 molecular weight as the standard, but Dr. Chou is using 40 000 molecular weight standard. Those dextrans found in the sugar mill are much much higher; over 2 million molecular weight.

Also, I agree with Dr. Matic; It may be not only the dextran, but there could be other things co-existing with dextran which contribute to the trouble. I feel that prevention of dextran should be going into the research program of the Project. Do we know the molecular weight distribution of dextran in the raw house? What kind of leuconostoc is producing these dextrans? What is their effect on viscosity? Which one is producing more elongation of the crystal? What is the mechanism of dextran formation? What is the length of time vs molecular weight, etc, etc.? One method of control is the use of biocides. If we know which molecular weight is more detrimental to refining, then we will have to look at what kind of leuconostoc we are trying to control, so that those who are suppliers of chemicals can look into what kind of biocide should be used for that kind of leuconostoc.

Now, of all these unsolved problems, I think that we need first of all to find out the molecular weight distribution of dextran in the raw house as well as in the refinery. Then we need a method of analysis, maybe for more than one range of molecular weights, which would be applicable to the raw house so they will know what method or what kind of control or what kind of additive will be effective so that finally their raw sugar will be more acceptable to the refinery.

M. A. CLARKE: I am glad that you brought out the point that there has been a great deal published in this area, particularly by the Australians, and the additional point that all work is not consistent in the answers to these points. There is no one answer that is satisfactory to everyone about the particular molecular weight ranges that affect the raw sugar houses and

the refinery. General opinion has it these days that higher molecular weight dextrans are problems in the mill and the lower molecular weight dextrans that are left once the mill gets the high ones out are the problem to the refiner. The low molecular weights are more soluble, depending upon their branching of course, and tend to go through into the final product.

I. SANGSTER (Sugar Industry Research Institute of Jamaica): Another comment, taking up Dr. Chen's point on co-existence of another species or factors with dextran: Occasionally in the raw sugar factories you have an explosive growth of leuconostoc causing rice grain. We have had it once or twice in Jamaica where the juice has actually gone solid in the tanks and you had to send men in with shovels to dig it out. At the Sugar Industry Research Institute, we have had a look at this when it has happened. On each occasion we have found a symbiotic mixture of leuconostoc, yeast, and a gram positive bacteria. This was also reported by the Australians in 1975. Dr. Matic's point was well taken that it may not be only leuconostoc itself, but another factor which occurs and is masked by leuconostoc. Certainly on this occasion it is a multiplicity of factors and three organisms.

R. KUNIN: I was rather surprised about the 1 out of 30 000 incidences in Europe of the fever problem arising from the use of invert and other sugar-bearing intravenous solutions indicating that it might be related to dextran. Since dextran comes from some microbiological process, there are probably billions and billions of pyrogen units present. It seems to me that intravenous solutions should be ultrafiltered or even filtered through a reverse osmosis unit because it would be the only way of removing the pyrogens. Even sterile solutions would still have a pyrogen reaction unless they were carefully filtered.

G. W. VANE: This incidence was that reported in Sweden, during a 7 month period in 1973; it was not stated whether the source sucrose was of cane or beet origin. The correlation was noted and published, (Int. Arch. Allergy Appl. Immun. 50, 606-612 (1976)). It was further shown that where dextran was absent or only present in very minute amounts, the incidence of such reaction dropped to 1/600 000.

No doubt bacteria, pyrogens or other such contaminants are present in sugar products, but most will not survive the process conditions involved. Ultrafiltration would indeed seem a wise precaution for such applications but it probably seems simpler to conduct a simple screen for dextran or - even worse - use a beet sugar shown to be free of dextran.

M. A. CLARKE: There is a political tinge to this finding, and to the regulations subsequently engendered by this work. Beet

sugar solutions used in this way do not contain dextrans; therefore, beet sugars and not cane sugars are approved for this use by the European pharmacopoeia.

E. MULLER (Tate and Lyle): After this problem arose with the European pharmacopoeia, I had negotiations with them about this pointing out that in no way could any cane sugar pass their test. And they eventually agreed for the future revision of the European pharmacopoeia to have 2 monographs for sucrose; one specifically for parenteral use where the "foreign sugars test", which effectively discriminates against dextran, was going to remain. But there was also to be a monograph for other sucrose, i.e. for eating, where the "foreign sugars test" was not going to be included. So, we hope that in this way the bulk of the sugar we sell, except that for pharmaceutical use, will in fact be all right.

K. IVIE (Waters Associates): Recent developments in liquid chromatography have tended to indicate that dextrans can be analysed on ion exchange resins. They elute first in the chromatogram and they can be quantified with a peak. There have been several examples of this preliminary work in South America. We have shown this with several companies we have been working with as well as the corn syrup industry where they look at higher molecular weight sugars and get quantities quite precisely; within 0.01% in many cases. What do you feel would be the advantage of using a technique like this that is specific for the high molecular weight sugars and can be used to quantitate them? One other thing we do know is that for degree of polymerization above 10 to 12, the response factor for the dextrans up to about 2 million remains constant on a refractive index detector.

E. J. ROBERTS: I agree that HPLC may become a very useful and practical method of analysis for dextran within the next few years.

H. R. DELANEY: I was very interested when I saw in the program that dextran was to be discussed. It surprised me a little actually; I had to get out our old reports to see what we had done. A lot of people here have referred to our work and basically it did originate with chopper harvesting in the mid to late 60's. The alcohol haze test was our development.

Dextran is rarely a problem today, which shows that the problem can be cured. You might ask how we did it? Basically, the way we did it was to cut down cane delay from harvesting to processing. This, of course, reduced the time in which infection by leuconostoc could occur. Also during our milling process there was a lot of attention paid to hygiene. We did develop enzymatic techniques to control dextran. Unfortunately by the time they were developed, which was the early 70's, we had overcome the problem by reducing cane delay. The work was

published (Hidi, Staker. QSSCT 1975: 331-343) and was left at that stage because we had solved it.

Can this reduction in cane delay be applied in the rest of the world? I have had experience in Fiji which is not anywhere near as mechanized as Australia, which is now 100% chopper harvested. The harvesting and rail systems are quite stringently controlled. I can see how in some areas of the world it would be an impossibility to reduce cane delay to the extent that you have to. I suppose that some of the other techniques that we began to look at are going to have to be applied. Unfortunately, this whole area of research is in abeyance, or at least at low level. Basically we have solved our problem and hopefully the rest of you will be able to also.

ANALYSIS OF CARBOHYDRATES BY HIGH PRESSURE LIQUID CHROMATOGRAPHY

Margaret A. Clarke and Mary Ann Brannan

Cane Sugar Refining Research Project, Inc.

INTRODUCTION

Classical methods for analysis of sugars and other carbohydrates have well-known shortcomings, generally because the analyses are of properties rather than compounds and therefore are subject to multiple interferences, often of unknown origin. In an effort to devise specific analyses for sugars and substances important in sugar processing, CSRRPI has investigated high pressure liquid chromatography techniques. HPLC offers speed, simplicity and versatility. This latter is especially important for laboratories with limited funds for equipment. This paper will discuss HPLC methods for sucrose, glucose and fructose, other sugars, sugar breakdown products and microbiological byproducts such as colorants and organic acids, and polysaccharides (dextrans, starch and sugarcane polysaccharides).

In most of these analyses, the sample is made into a solution of suitable concentration, filtered, and injected directly into the HPLC instrument. This simplicity of preparation is very suitable for process control work.

SUGARS

Since 1976, this group has published several papers on the use of HPLC for analysis of sucrose, glucose and fructose (Clarke et al. 1977, Clarke and Brannan 1978a, 1978b, 1978c, Clarke and Brannan 1979) in raw and refined sugars, process liquor and molasses. The limits of accuracy of the technique are met in analysis of refined white sugars, where the small amounts of non-sucrose compounds are difficult to detect without preparatory separation from sucrose. Raw sugars can be analyzed satisfactorily (Clarke and Brannan 1978c), although two steps are required: one for sucrose, and another for glucose and fructose, because of the order of magnitude of difference in concentrations. HPLC is ideally

suited for analysis of cane juice (Wong-Chong and Martin 1980) and molasses (Clarke and Brannan 1978). Our method for sugars in molasses has been adopted, with some modifications by the U.S. Bureau of Customs (Damon and Pettitt 1980), and is used there as a routine analysis for molasses. Because HPLC shows the concentration of sucrose, glucose and fructose individually, these levels have been revealed to be lower by several percent than those shown by polarization or copper reduction methods in molasses.

The analysis of molasses leads to fermentation - an important development to many areas of the sugar industry. HPLC analyses for sugars are especially useful here because they give a true picture of sugars available for fermentation. It is now possible, with special columns and low pressure techniques to analyse for sugars, dextrins, and alcohols in one process (Ladisch and Tsao 1978).

HPLC is used reguarly for analysis of sugar blends (Brobst et al. 1973, Fitt et al. 1980) and is a routine analysis for producers of high fructose syrups and their customers.

Column technology has changed over the past few years. In all sugars analysis, detection is by differential refractometer, but the separation mechanisms vary. Early work by this group (Clarke et al. 1977, Clarke and Brannan 1978a) used a microparticulate column of polysilane-silica, bonded to an active amine compound (Waters Associates u-Bondapak carbohydrate), with an acetonitrile-water solvent. Recently, ion-exchange based columns have been more satisfactory and currently offer the best quantative analysis for sugars (Bio-Rad Aminex HPX-87) using water only as solvent, and operated at a temperature of 80°C (Clarke and Brannan 1979). It is possible to buy this column already prepared or to purchase similar resins and pack columns in the laboratory (Wong-Chong and Martin 1980).

The latest development is use of a short, relatively cheap, silica column used with a radial compression device that packs the column in situ. The column is treated with a complex amine compound dissolved in the solvent of acetonitrile and water (Wheals and White 1979, Day 1980). This amine modifies the column so that it will separate sugars. A quantitatively satisfactory separation can be achieved of mono-, di- and tri-saccharides in about 10 minutes as shown in Figure 1. Until this new technique, trisaccharide analysis on regularly available columns required some 30 minutes. This technique has the advantage of cheap columns, speedy analysis, and room temperature operation. The radial compression treatment requires the purchase of an additional piece of equipment; however, this device can be used with the addition of solvent modifers, to

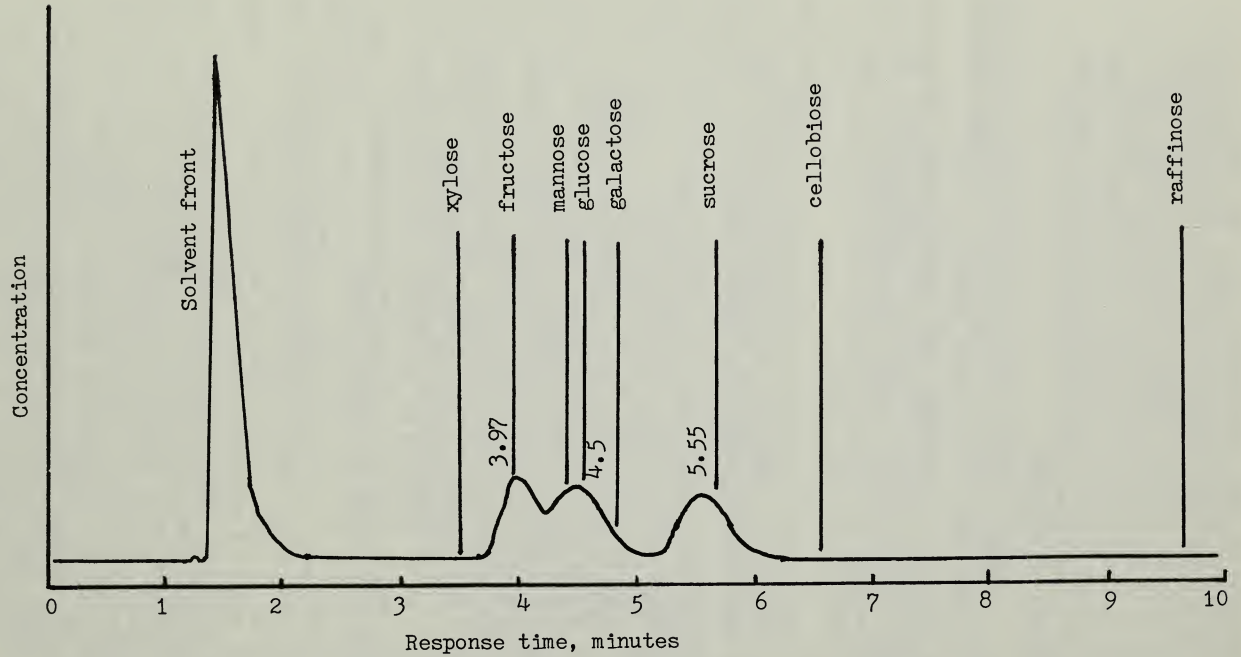

Figure 1.--HPLC of sugars on a radially compressed silica column. Only fructose, glucose and sucrose were in the sample. Positions of other sugar peaks are indicated.

prepare columns for almost any other separation so that prepared columns, e.g., reverse phase columns, need no longer be purchased.

Table 1 shows conditions for the various types of sugar analysis.

ORGANIC ACIDS

Lactic Acid

We have found that lactic acid can be analyzed on the same HPLC resin column used for sugars analysis. Lactic acid elutes just after fructose, in the same area as monosaccharides on the Bio-Rad HPX-87 column. Lactic acid is a byproduct of bacterial (Lactobacillus) action on sugars, and is particularly important to beet sugar manufacturers. It is also important in fermentation, because bacillary action occurs along with yeast growth, using up the necessary sugars. Lactic acid reduces copper, in copper reduction

Table 1.--HPLC of sugars: conditions

Comments	Column	Solvent
	μ-Bondapak carbohydrate	Acetonitrile-water. Room temperature
Currently best available	Aminex HPX-87 or other resin. Prepared, or homemade	Water. 80°C
Prospective best	Radially compressed silica, with TEPA	Acetonitrile-water. Room temperture
For molasses	Partisil-10 PAC-25	Acetonitrile-water Room temperature.

titration analyses, e.g., the Lane-Eynon procedure, and can confuse results on analysis of reducing sugars - important in analysis of available sugars in biomass for fermentation. Sugar alcohols can also be analyzed by this technique on the same column, and in the presence of sugars (Davis and Hartford 1979).

Aconitic Acid

The classical method for aconitic acid involves a lengthy and complicated decarbonxylation titration, often after extended sample drying (Ambler and Roberts 1947). We have worked out an HPLC method, using an ethyl acetate extract of raw sugar on cane juice, run on a reverse phase column (μ-Bondapak C-18), with detection by U-V light of 254 nm. The whole procedure takes about 40 minutes, and agrees within 10% with the classical method.

Aconitic acid is sometimes a major contaminant in raw sugar production, especially from young cane. It crystallizes with the sugar. It is a problem in production of sugar from sweet sorghum. Table 2 shows conditions of analysis for both aconitic acid and lactic acid.

Table 2.--HPLC of organic acids: conditions

	Lactic acid	Aconitic acid
column:	Aminex HPX-87	μ-Bondapak C-18
solvent:	H_2O, 80°C	5% acetic acid in H_2O, room temp.
detector:	Differential refractometer	U-V, 254 nm
sample:	Aqueous solution of sugars, cane juice, or fermentation medium.	Ethyl acetate extract of raw sugar or cane juice.

COLORANT AND COLORANT PRECURSORS

HPLC techniques can be used to examine "color" in general (Smith 1977). Our laboratory has worked out a procedure to survey colorant in sugars and changes in that colorant under storage. An ethyl acetate extract of raw or refined sugar is run on a reverse phase column, with a solvent gradient of methanol-water as outlined in Table 3. A complex chromatogram is obtained. CSRRPI has been storing a series of sugars (several raws of varying quality and a very good refined sugar) for over a year, at 100°F, removing samples each month. HPLC analysis reveals changes in the colorant in these sugars over the storage period.

Table 3.--HPLC of whole colorant: conditions

column:	μ-Bondapak C-18
solvent:	Gradient of methanol and water + acetic acid
detector:	U-V, 254 nm
sample	Ethyl acetate extract

In order to elucidate the complex chromatograms of whole colorant, individual compounds known to contribute to color or color formation have been analyzed. A list of these compounds and their method of analysis is given in Table 4. Several of these compounds are organic acids but are included in this section because of their relation to sugar color,

Table 4.--HPLC of colorant compounds and precursors

Compound	Conditions
fumaric acid 3,4-dihydroxy benzoic acid p-hydroxybenzoic acid gallic acid levulinic acid vanillin maltol imidazole furfural acetyl furan furfuryl alcohol 2,5-dimethyl pyrazine caffeic acid chlorogenic acid quinic acid syringic acid ferulic acid sinapic acid umbelliferrone	column: μ-Bondapak C-18 solvent: 5% acetic acid in water detector: U-V, 254 nm sample: Ethyl acetate extract of sugar

e.g., levulinic acid, the hydroxybenzoic acids and gallic acid. Other workers have devised HPLC analyses for Maillard reaction product compounds (also part of sugar colorant) (Takeoka et al. 1979).

In addition to these many compounds, an HPLC method for 5-hydroxymethyl furfural (HMF) has been developed. HMF is an important intermediate compound in the formation of color from sucrose decomposition under conditions of heat and/or low pH. The presence of HMF indicates that color will soon follow. The HPLC method, using a reverse phase column, is outlined in Table 5. A solvent gradient of methanol/water was used initially, but it was found that water alone gave a satisfactory chromatogram. Submicrogram quantities of HMF can be detected easily. A high-grade refined white sugar, that initially showed no traces of HMF, after being heated at 110°C for 24 hr showed considerable HMF presence although the white sugar visually observable color had darkened very slightly at that time. Quantitative measurement of this HMF was not done, because some of the decomposition products of HMF were also observed on the chromatogram. The sugar darkened considerably after several more days at room temperature. This HMF measurement may offer an indication of color problems to be expected in storage, or offer evidence of poor storage conditions.

Another example of the use of HPLC in color work is in the analysis of color compounds in our sugar boiling studies. HPLC techniques have been used to analyze the non-sucrose compounds in the crystal and syrup produced by the model vacuum pan (Devereux 1980).

POLYSACCHARIDES

Our work with polysaccharides separation and analysis is in the very early stages. By using a gel permeation type column, which separates compounds on the basis of their molecular weights, and a variety of solvents, we have found

Table 5.--HPLC of HMF: conditions

column:	μ-Bondapak C-18
solvent:	Methanol-water gradient or water alone, R. T.
detector:	U-V, 254 nm
sample:	Ethyl acetate extract

initial indications that it will be possible to separate dextrans, starch, and ISP and other sugarcane polysaccharides. The sugar industry has a great need for rapid methods of separation and analysis of these troublesome high molecular weight compounds.

SUMMARY

High pressure liquid chromatographic analysis is a useful tool for sugar processing. Sugars can be analyzed individually and rapidly, in a single determination. The time of the analysis approaches that of a polarization determination, but the accuracy must still be improved. (The accuracy of polarization is under the assumption that only sucrose and known invert polarize). The time of an HPLC analysis for sucrose and reducing sugars is much less than the time required for a polarization plus a reducing sugars determination, and the overall accuracy here is at least comparable to that of classical methods for all but the highest grade sugars, and better than that of classical methods for molasses and low grade syrups, and probably for effluent streams. HPLC offers the ability for rapid analysis of aconitic acids, problem compounds to some areas of the sugar industry.

Colorant, and many colorant compounds and color precursors can be measured by HPLC techniques. HMF, a particularly useful indicator of color formation, is easily observed.

It is expected that polysaccharide separation and analysis can be simplified by HPLC techniques.

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DISCUSSION

K. IVIE (Waters Associates): I can't speak much about sugar cane technology. We have just started working with the cane industry, although we have worked with CSRRP for quite a while and they are a long way ahead of most people in the world in terms of HPLC with cane products. Recently we have begun working with LSU on sugar cane. But what we are finding is that the problems that are faced in the cane industry are very similar to the problems that we have already solved in the corn syrup industry. Although the compounds are slightly different, the technologies that are being applied to resolve them are very similar. One of the things that was aluded to was that the precision was not quite there yet. The corn syrup industry has been working with LC now for 6 years. A recent paper by Scobel, et al (J. Am. Assoc. Cerial Chem., 54, 905-917) is reporting relative standard deviations of 0.15% on individual sugars for an automated analysis. This is a very precise analysis. Recoveries of sugars out of matrices has been shown to be 100% with a relative standard deviation on recoveries of 0.1%. Compared to polarization that may sound like a big error, but the polarization technique can be precisely inaccurate. It can have 6 decimal places in precision and be as much as 3% off in accuracy. In such a situation the 6 decimal places don't mean a lot. We are striving to bring the kind of precision that we have found in the corn industry down to the cane applications. We havn't gotten there yet because it is a new field, although the samples are similar and the problems are the same in terms of types of compounds, there are slight differences in sample preparation, dilutions, and other aspects of the technology.

H. R. DELANEY: We are doing a lot of work that parallels yours. In your polysaccharide work I see that you are using a pretreatment and then a separation. But, I wonder what standards or known reference materials you are going to use, especially when you look at ISP and dextrans. You are going to get quite a lot of peaks and you have a problem of what they actually are. A lot of these things are not available commercially as known pure compounds. How do you plan to treat that problem?

M. A. CLARKE: As you say, known standards are not available for many compounds. We have found that even the commercially available dextrans are not pure, and often contain several percent mannose (mannans). We will have to use regular gel permeation, or ultra filtration, and make our own standards.

H. R. DELANEY: This would group a lot of things together according to molecular weight.

M. A. CLARKE: We would hope to have an additional basis for separation than molecular weight alone. This will require a different column material and different conditions. We have not yet succeeded in doing this, but we do have some hope.

M. C. BENNETT (Tate and Lyle): Would you elaborate on the use of HPLC to measure HMF? That was a very interesting experiment that reveals the power of the approach. Presumably what you did was take that granulated sugar, cook it up and then just leave it lying around. What you wanted to do was just see what was happening while it was lying around. I assume that you can do the same thing with a raw sugar as delivered. This might be a very valuable analysis that the refiner might make use of, giving him fair warning of a particular raw that has an in-built load of problems which you would not detect by any other means. Specifically, does the HMF peak disappear as the color forms?

M. A. CLARKE: That depends upon the conditions under which the sugar is held. Yes, the HMF peak disappears as the color forms because HMF is reacting to become color molecules. However, HMF can be forming from sucrose at the same time if the sugar is rather warm and rather wet. It is not a static situation. However, if you know that the sugar is not going to be held at high temperature under high moisture conditions, then you don't have to be particularly concerned about more HMF forming, and you can say HMF is disappearing because color is forming. We did look at raw sugars as well as refined sugar. The refined sugar was rather more dramatic to observe, but the same thing does happen with raw sugar.

The analysis for HMF takes about 20 minutes to make an extract, and 10 minutes on the instrument, for 30 minutes total time. Water is the solvent. This will certainly be a useful analysis and is something we want to continue to develop.

C. C. CHOU: If you use a gel type column which is based on molecular weight for separation, it would be difficult to separate dextran from other polysaccharides. One way you could do it would be to run the sample with and without dextranase treatments. The difference in area under the peaks would represent the dextran in the sample.

M. A. CLARKE: That is a possible approach. We started to do

that, but there are a few problems using that approach. One problem is that the dextranase is in the sample too: it is a high molecular weight compound and cam appear in the peak for high molecular weight material. Another problem is that dextranase usually does not break the high molecular weight compounds down into single glucose units: it breaks dextran down into smaller polymers of glucose. I was surprised to see, yesterday, in your paper, that you got results of zero dextran after dextranase treatment. Perhaps you allowed sufficient contact time for the enzyme to break all the 1-6 linkages. A third problem is the dextranase enzyme itself. You can't get pure dextranase in this country; the Novo Company was the only source and there wasn't enough market for them to clear it with FDA for food use. So, they are not going to sell it. What dextranase we have got has been sent to us by people in other countries, and it has not been very pure. There are amylases, galactosidase and other enzymes in it.

We are taking other approaches now to have other bases upon which to separate these high molecular weight compounds. We know for example, that ISP has acid groups on it, and so might use that property to separate ISP from other polysaccharides. We do not expect to separate them on a molecular weight basis alone.

M. MATIC: In the storage of raw sugar, the color development is not in the crystal but in the syrup coating. The amount of color produced in the crystal is very small. Have you been working on the molasses film or the whole sugar?

M. A. CLARKE: Yes, the color forming reaction is entirely in the coating. Water is needed for the reaction. You see the color in the whole sugar but much of the color would come off in affination, at least for those refiners - the majority - who still use affination.

M. MATIC: Mike Bennett thought this would be a useful method for the refiner to see what he could expect from the raw sugar, but most refiners are interested in the crystal color and not in the molasses color.

M. A. CLARKE: When you have a recovery house, you are also interested in the molasses color, and in the color in affination syrup.

M. MATIC: I agree with that.

ACTIVITIES OF THE SUGAR INDUSTRY RESEARCH INSTITUTE (FACTORY TECHNOLOGY DIVISION)--JAMAICA

Ian Sangster

Sugar Industry Research Institute (Factory Technology Division)--Jamaica

HISTORY OF SUGAR PRODUCTION IN JAMAICA

During the 18th century, Jamaica had over 800 small sugar factories, using wind, animal or water power to drive simple mills. In 1805, the island's sugar production was 100,000 tons, making it the world's leading producer. From this time, there occurred a gradual reduction in the number of sugar factories, as technical progress stimulated a reduction in the number of production units, with a corresponding increase in the size of the remaining factories. These demanded staff with ever-higher levels of technical skills, and were thus responsible for a very important 'transfusion' of modern skills to rural areas all over Jamaica in the form of engineers chemists, mechanics, electricians, agronomists, etc.

From 65,000 tons of sugar in 1930, Jamaican production soared to 270,000 tons in 1950. This increase was largely due to the entry of the West Indies Sugar Company (W.I.S.Co.), a subsidiary of the British sugar producers, Tate and Lyle. It established the two largest factories on the island, Frome in Westmoreland, and Monymusk in Clarendon, with a joint capacity of over 180,000 tons of sugar per year. It would be difficult to exaggerate the impact on the Jamaican Sugar Industry of this giant company with its world-wide sugar experience.

Jamaica's highest ever sugar production was over half a million tons--506,000--in 1965, produced by eighteen factories. During this period Jamaica received a great influx from overseas, of the technical skills necessary for the operation of giant central factories such as Frome and Monymusk, and this influx had a very beneficial effect on the entire Jamaican sugar industry, which was regarded as one of the most efficient and advanced in the world. It is important to remember however, that the majority of the technological skills were

'imported' in that the technologists and engineers were either expatriates or Jamaicans trained overseas. The Jamaican sugar industry had no difficulty in attracting skilled staff from overseas, and in retaining skilled staff.

THE PRESENT SITUATION

It is interesting to compare some of the key production and efficiency figures for the 1968 and 1980 crops, viz.:

	1968	1980
Tons sugar produced	457,000	242,000
Tons Cane/Ton 96° Sugar	9.46	11.01
Factory time Loss % Total Time	10%	12%

Clearly, our technological performance today is inferior to 1965, and this has a number of causes, e.g.:

a) Lack of reinvestment in factory equipment and difficulties in obtaining spare parts.

b) Quantity, quality and delivery of cane supplies.

c) Shortage of technical staff.

c) was caused by other industries, and more importantly,other countries, offering more attractive salaries and conditions to technologists with skills which were in international demand. The net result was a reversal of the technological influx which occurred between 1930 and 1950. This problem in Jamaica is by no means peculiar to the sugar industry, but sugar provides an excellent example of the fact that an industry's efficiency is largely determined by the level of technical staff it employs.

The number of sugar factories in Jamaica has fallen to twelve, six of which have associated distilleries. Eight factories, including the three largest, are government owned, and are operated by the National Sugar Company (NSC), which is a subsidiary of the government's Sugar Industry Authority (SIA). This authority was established to regulate and control the Jamaican sugar industry, including the operation of the Research Department of the former Sugar Manufacturer's Association. This long-established institution, located at Mandeville in the centre of Jamaica, dealt almost entirely with agricultural matters.

DEVELOPING COUNTRIES' NEED FOR TECHNICAL ASSISTANCE

There is clearly a need in many developing countries for technical assistance of a type which is relevant to their stage of development. This has not been appreciated by some

organisations and companies in developed countries, which has led to some unfortunate developments taking place where sophisticated technologies were introduced into countries which did not possess the infrastructure to support and maintain them.

Thus, where a developing country such as Jamaica establishes a research and technical training unit designed to be relevant to its own situation and needs, its programmes are also of particular interest to other developing countries. This is appreciated by Cuba, which offers "technical co-operation" agreements to sugar-producing developing countries throughout the world, on the basis that Cuban technology is more relevant to "fellow Third World countries", than is that offered by commercial companies and institutions in the developed world.

THE ESTABLISHMENT OF SIRI FACTORY TECHNOLOGY DIVISION

By 1974, the decline in the level of average factory performance had become so marked that it was decided to expand the Research Department into a Sugar Industry Research Institute, comprised of two separate and autonomous Divisions, one of which, located in Kingston, was to be responsible for the technical problems of sugar factories. This was named SUGAR INDUSTRY RESEARCH INSTITUTE, FACTORY TECHNOLOGY DIVISION and, for the first time, Jamaica had a centre responsible for technical development of all Jamaican sugar factories. This was a very necessary step, but taken at least ten years too late, and by late 1974, SIRI Factory Technology Division had a director and no staff. Today, just over five years later, we have a total staff of thirty, and have developed research and training programmes which, in addition to helping Jamaica's sugar industry, are attracting attention and support from all the sugar-producing countries of the English-speaking Caribbean, and also from many other parts of the world. Has the existence of this new facility had any noticeable effect on the performance of Jamaican sugar factories? A look at Jamaica's production of commercial sugar from 1974 to 1980 (see Figure 1), would indicate a definite effect, as sugar production has declined steadily since the establishment of the Division! However, this conclusion would be as justified as a honeymoon couple aboard the Titanic assuming that they were to blame for the sinking, as so many factors not related to factory technology (especially cane quantity and quality) have contributed to this decline. Once an industry has been allowed to decline to below certain critical levels, it takes a long time to bring it back up to its former position.

Beyond the critical point several factors come into play, including:

a) Unless there is centralised training of new entrants to the industry, the "threshold training" of recruits is dependent upon the sugar factories

having sufficient competent technologists, engineers and tradesmen to train recruits. Given a chronic shortage of competent professionals, the later generations will be ever-fainter copies of poor originals.

b) As the number of competent technologists/ engineers decreases, greater strain and responsibility is thrown upon those remaining, giving them less time to assess and try new technologies, thus increasing the probability of their departure also.

SIRI, in its five years of existence then, has given a transfusion of training and technology to a haemorrhaging patient, which has assisted in keeping it alive. The causes of the haemorrhage however, are more political/economic than technical, and the sugar industry has resembled a cork bobbing on the waves of political change in Jamaica. We are, however, now in a position to train young technologists and to develop programmes to suit our own needs.

For every trained technologist we now have several younger ones in training, and hope to retain the older ones for as long as possible, so that their knowledge and experience can be passed on to the next generation.

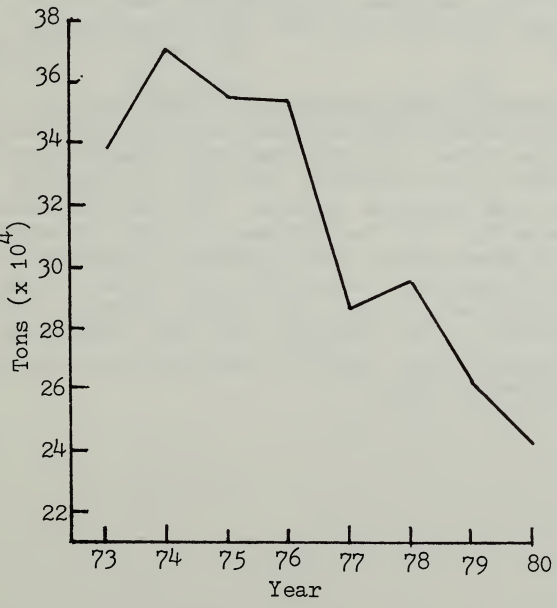

Figure 1.--Jamaican sugar production 1973-1980

DETAILS OF SIRI (FACTORY TECHNOLOGY DIVISION) ACTIVITIES

1. Technical Training

SIRI offers a wide range of courses from a Post-Graduate Diploma Course of two years' duration (run in conjunction with the University of the West Indies (UWI), through a lower-level one-year course run in conjunction with the College of Arts, Science and Technology (C.A.S.T.) down to on-the-job training of sugar factory workers in all areas of factory operation. There has been a steady increase in commitment to technical and scientific training programmes over the past four years and an even greater increase is projected for 1980/81. Since the commencement of out-of-crop residential training in 1975, participants have been enrolled from other Caribbean countries for these short courses, and the indication are that this participation will increase.

In 1979 the Institute first accepted trainees from the continent of Africa with the enrolment of five engineers and one chemist from Tanzania for the full-time training programmes. In 1980/81, there is an increased enrolment of seventeen foreign trainees drawn from Tanzania, Nigeria, Trinidad and Barbados. Following discussions with the European Economic Community's Directorate for Development, the Institute's full-time courses are recognised as approved courses for the purpose of the award of the studentships under the ACP/EEC (Lome 11) Agreement. Applicants accepted by the Institute for such courses are eligible for these awards, and ACP sugar-producing countries have been notified of this.

Table 1.--Growth from inception of the Institute
See bar chart (Fig. 2) for further information

		1975 76	1976 77	1977 78	1978 79	1979 80	Proj. 1980 81
Out-of-crop residential	Personnel	90	97	119*	248	124*	250
	Man-weeks	200	180	253	430	260	450
In-service training	Personnel	-	124	175	538	677	900
	Man-weeks	-	167	350	1,638	2,277	3,000
UWI/SIRI Post Grad Diploma	Personnel	-	Pilot Scheme 4	5	7	6	8
	Man-weeks	-	196	245	343	294	392
SIRI Factory Engineer's Cert.	Personnel	-	-	-	3	18	12
	Man-weeks	-	-	-	96	576	384
CAST/SIRI Sugar Tech.	Personnel	-	-	6	-	-	10
	Man-weeks	-	-	294	-	-	490

* Courses mainly for supervisors.

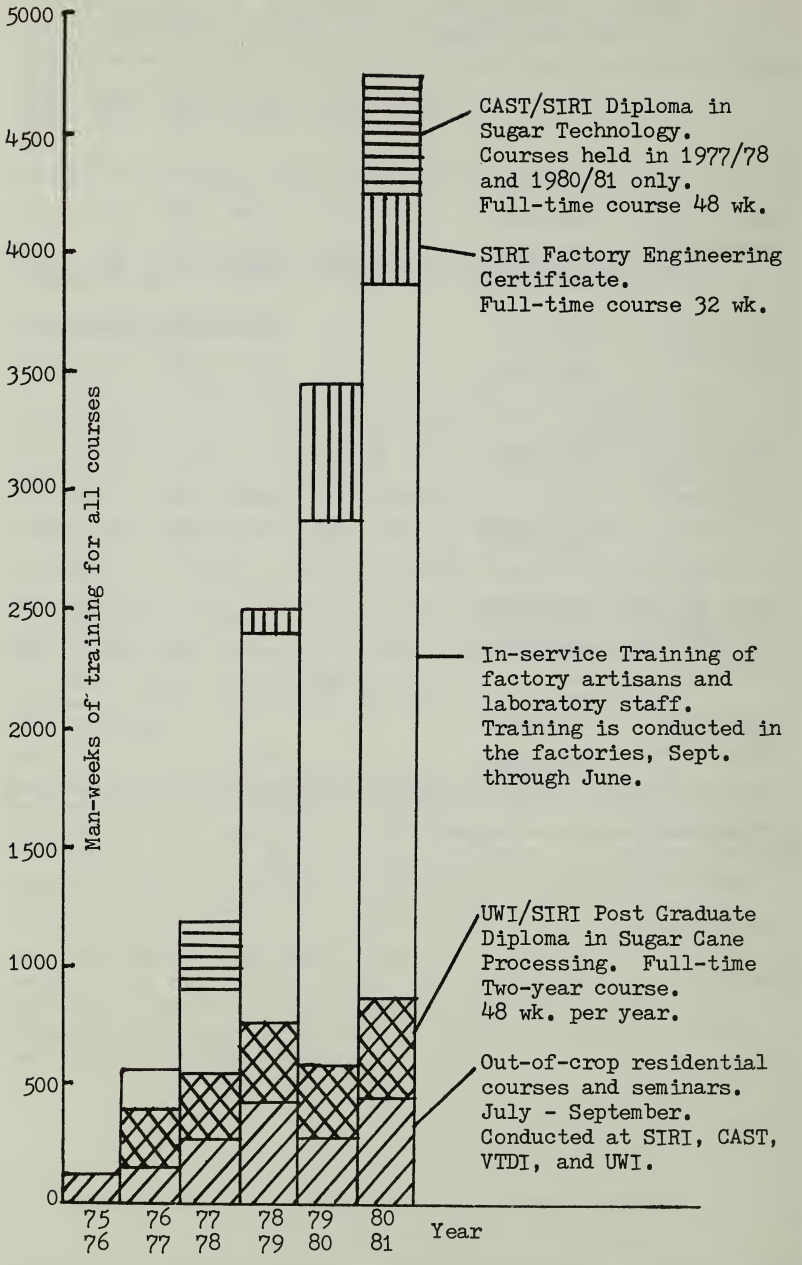

Figure 2.--Sugar Industry Research Institute (Factory Technology Division). Chart showing growth of technical training programs since the inception of the Institute.

Out-of-Crop Residential Courses

The out-of-crop period coincides with the summer vacation of CAST, thus enabling SIRI to use virtually all the facilities of the College for the period July - September These facilities include workshops, laboratories, lecture-theatres, accommodation, canteen, etc. Sugar Factory Personnel are brought into CAST for a wide range of courses, (e.g. in 1979, 248 people received 430 man-weeks of training).

In order to build up a cadre of highly skilled artisans within each factory, we have attempted to link the in-service training programme with the out-of-crop residential training, so that the factory employees who show good potential for learning can have advanced intensive training during the out-of-crop courses. By this means, it is hoped to create skilled groups within the Industry capable of teaching their fellow-workers in the factories. Training Officers propose to factories which artisans should be sent on out-of-crop courses.

Table 2.--Out-of-Crop Residential Courses (July/Sept.) 1980

	Course Designed For	Duration (days)
* Laboratory Technicians (Year 2 of a 3-year Course)	19	21
The Technology of Sugar Cane Processing I	12	14
The Technology of Sugar Cane Processing II	12	14
Machine Shop Engineering	12	14
Petrol and Diesel Engine Operations & Maintenance I	12	14
Petrol and Diesel Engine Operations & Maintenance II	12	14
Automotive Electrical Systems	12	7
Advanced Course in Electrical Motor Control	12	14
A.C. Generators	12	14
Advanced Instrumentation	10	14
Bagasse Fired Boilers (Factory Engineers)	20	7

Table 2.--Out-of-Crop Residential Courses (July/Sept.--Continued

	Course Designed For	Duration (days)
Pumps and Pipe Lines	12	14
Transport Managers' and Supervisors' Seminar	15	4
Technical Drawing	6	21

2. Technical Services to Sugar Factories

SIRI provides a technical advisory trouble-shooting service to all Jamaican sugar factories.

The main areas of activity are:

a) Energy Conservation. As the main thrust of SIRI's Energy Conservation Programme, a "Boiler Task Force" was formed during the 1979 sugar crop to reduce the appallingly high level of fuel oil burning in the Government-owned sugar factories. For the 1980 crop, the Task Force was given responsibility for boiler operation at Bernard Lodge sugar factory, which during the 1979 crop had burned 100 gallons of fuel oil for each ton of sugar made. For the 1980 crop this was reduced to 40 gallons/ton sugar, which is still much too high, but nevertheless effected a saving of US$1.1 million for the factory, for the crop.

b) Process Technology. Routine industry-wide tests are made of cane preparation, milling efficiency, sugar recovery, pan floor operation, etc.

c) Instrumentation. New equipment or techniques are tried out at the SIRI Pilot Plant and if approved, are given industrial trials in a sugar factory. By this means a much higher level of instrumental control is being introduced into our factories, e.g. fourteen DDS pan-boiling control systems are now installed and working satisfactorily in Jamaican factories.

d) Laboratory Operation/Chemical Control. The Institute runs a Control Analytical Laboratory located on the U.W.I. campus, which analyses all local and export Jamaican Sugar for pol, moisture, insolubles, grist, colour, etc. Spot checks are made on sugar factory laboratories, and a repair and calibration service for

optical and electronic lab. instruments is offered to all sugar factories. The standard of factory laboratory staff leaves much to be desired, and intensive training programmes have been implemented, involving in-service, residential and correspondence courses.

All SIRI technical training staff pay regular visits to all Jamaican factories, and a report is submitted to the factory after each visit. Thus, by spreading its technical staff thinly over all 12 sugar factories, SIRI helps greatly to compensate for the shortage of technologists and engineers in the Jamaican Sugar Industry.

3. Research Programmes

It is difficult for small industries to justify expenditure on fundamental research, and so it is with SIRI. Most of the sugar technology research carried out is very applied, involving essentially the assessment of new (to Jamaica) techniques or equipment, and its suitability for the Jamaican Sugar Industry. However, we have one major exception to this general rule. This is an examination of the potential of the Cane Separation Process (also known as "Comfith"). This technique splits individual cane stalks down the middle and then separates the finely divided (over 90% cell breakage) cane interior from the intact outer rind. Over 90% of the sugar is thus easily recoverable (by milling/diffusion) from the interior "pith" and the intact rind strips are a very tough and strong material offering exciting possibilities for manufacture of a range of particle boards, after removal of the outer waxy layer (so-called "Dermax").

The various products of cane separation form the basis of research programmes at SIRI, viz.:

a) The Rind. Work on a laboratory scale has resulted in the production of various types of rind board, e.g. decorative panelling, and structural boards up to three inches thick. Due to physical restrictions these have been made in six-inch square samples. The technology is fairly straight-forward, involving the application of pressure and heat with resin bonding.

b) The Dermax. Work is proceeding under supervision from the Institute, in the Chemistry Department of the University of the West Indies, to determine the best and most economical method of extracting the wax from the dermax with the objective of producing a refined wax.

c) The Pith. With the extremely high cell breakage, juice extraction from the pith is much simpler than from whole chopped cane and the energy required for

this process is greatly reduced. In addition, a much cleaner juice is obtained by virtue of the removal of the outer rind. Work is proceeding on the production of various types of sugar from this juice, e.g. an amorphous golden sugar containing the total solids of the clarified cane juice. The spent pith, after removal of about 97% of the sugar, is being investigated as the basis of a feed for ruminants. This involves the physical/chemical treatment of the pith to increase digestibility, and incorporation in a total feed consisting of 45% pith, molasses, soya meal, urea, and a mineral/vitamin supplement. Results on dairy cattle over a period of twelve months have been encouraging, and much more extensive trials on both beef feedlot and dairy cattle are about to begin.

A CENTRE FOR THE DEVELOPMENT OF SUGAR INDUSTRY BY-PRODUCTS

The Institute now intends to proceed to the semi-commercial development stage with the production of animal feeds and particle boards, and to develop fermentation and distillation technologies, coupled with biogas generation. An integrated plant for the development of Sugar Cane By-products is necessary and will be located adjacent to the Sugar Technology Pilot Plant.

It is intented to proceed with the following projects at this plant:

a) Animal Feeds. For cane pith and/or bagasse a wider range of treatments needs to be studied, and also the development of optimum complete rations based on treated pith or bagasse, utilising the maximum content of local ingredients. It is intended to produce this feed in pelletised form.

b) Particle Board from Cane Rind. Standard ten-inch and twenty-four-inch square interlocking decorating panels will initially be produced. Parquet type floor blocks, structural members, and panels for low-cost housing construction will be investigated. Durability and strength testing will be completed in co-operation with the Jamaican Bureau of Standards.

c) Fermentation Technology. Initially the study of modern and more efficient methods of alcohol production from sugar cane juice or molasses (e.g. continuous or heterogenous fermentation, fast, thermophilic, high alcohol-tolerance yeasts, etc.). Later, the study of hydrolysis and fermentation of cellulosic raw materials as sources of alcohol.

(d) Distillation Technology As a complement to (c) to study modern techniques and possible small-scale novel techniques, such as membrane separation of alcohol from water.

(e) Biogas Generation The effluents from distilleries, e.g. dunder(also called 'stillage') and settled yeast cells are environmental pollutants. They can, however, be used to generate Biogas to supplement the energy used to operate the distillery. Pilot Plant scale research into methodology is required.

Developed together, as an integrated system, the above projects could enable a small to medium scale manufacturing complex to be developed which would produce animal feeds, power alcohol and low-cost building materials from sugar cane, and perhaps be totally energy-self-sufficient. This would have application to areas under sugar cane cultivation which are distant from the nearest central sugar factory, and whose cane becomes uneconomic because of rising transportation costs.

DISCUSSION

M. A. CLARKE: Do you have any yield figures from the Comfith cane compared to cane in a regular mill train?

I. SANGSTER: It varries with variety. Between 5 and 10 % of the sugar is with the rind. The rest is in the pith in a very easily extractable form.

M. A. CLARKE: You usually got 220 pounds of sugar per ton of cane by regular milling. What would you get from Comfith?

I. SANGSTER: You get more out of pith than you get out of an equivalent weight of whole bagasse. We probably loose 5 to 10 % of the total sugar, but it is still in the rind.

M. A. CLARKE: And there is much less milling and processing required to make sugar from the pith?

I. SANGSTER: The energy is about 30% less than conventional milling.

M. A. CLARKE: In regard to your bagasse-based cattle feed: do you mix that with urea and molasses or do you feed it straight?

I. SANGSTER: The standard ration is 40% treated pith, 30% molasses, 27% soya meal, 2% urea, and 1% mineral and vitamine supplements. It is a whole feed. We are interested in using distillery products such as yeast for cattle feed. Unfortunately, our fermentor bottoms have a very high inorganic content, which causes problems when used as a feed. The basic cause is that none of our distilleries treat their molasses. We are getting one distillery now convienced to treat their molasses and we are going to try some yeast feeding trials on that.

M. C. BENNETT (Tate and Lyle): Most of us are aware of the potential for saving energy in the Comfith machine. What scares so many people who have seen it is the degree of preparation and care you have to take with the cane supplies. If you let stones get anywhere near that blade, the machine breaks. What lengths do you have to go to in practice to clean the cane, make sure that it is in straight, short lengths, and eliminate stones?

I. SANGSTER: The stones are no problem because we have hand cut and loaded cane at the pilot plant. We have a little feeding device with fingers that pick up the cane in whole stalks. They are fed in rather like a machine gun, at 26 ft/sec. These mills are very small and the tolerance is 0.032 inch. The blades are high tensile stainless steel. If anything, stone or iron, goes through, they break. In fairness I must say that if it breaks, it is only a work of minutes to pull out one of the small mills. The technology is rather like a machine gun vs. a connon. Instead of having one huge mill, you would have several Comfith machines running in parallel. If one breaks, others would still be working while you are changing the roller. I would think that standard chopper harvested cane would be an almost ideal feed material.

The maximum feed rate achieved up to now is 40 tons per hour with chopper harvested billited cane. The question is, how long can they keep it up? 40 Tons per hour for only 1/2 hour doesn't help much. This has to run for 24 hours every day. This is the question the engineers have to answer on this machine. Two groups are working on it; Hawker Siddeley and Intercane, both Canadian. They are putting a lot of effort and money into it.

F. G. CARPENTER (Southern Regional Lab.): In a beet operation a stone will break their blades too, but the slicers are designed so that the blades can be changed in a few seconds. The fragile part of the Comfith machine seems even simpler than a beet slicer, so a little development should make this problem only and anoyance.

DECOLORIZATION AND CLARIFICATION OF CANE SUGAR SYRUPS BY MEANS OF POWDERED ION EXCHANGE RESIN TECHNOLOGY

Robert Kunin and Al Tavares

Graver Water Division of Ecodyne Corporation

INTRODUCTION

It is of interest to note that the technologies of sugar refining and ion exchange have been related to and dependent upon each other for approximately eighty years. Each major development in ion exchange technology has received considerable attention by the sugar refining industry including the cane, beet, and corn sugar sectors. As a result, ion exchange technology has become well established throughout the sugar refining industry for the following functions:

1. Decolorization
2. Deashing
3. Softening (Calcium removal)
4. Catalysis (invert formation)
5. Chromatography

In the area of cane sugar refining, ion exchange technology has been employed on a serious level for decolorization of syrups prior to the sucrose crystallization operation and for the decolorization and deashing of liquid syrups. Over the years, as ion exchange technology has developed, it has become established throughout the world as a sugar refining aid, particularly as new and improved ion exchange resins have evolved. In many areas, ion exchange resin technology has implemented and, on occasion, replaced the various carbonaceous adsorbents such as bone char, granular activated carbon (GAC), and powdered activated carbon (PAC).

The use of ion exchange resin technology for the decolorization and deashing of cane, beet, and corn sugar has been thoroughly documented in the literature (Conklin 1959, Andrus 1967, Kunin 1968, 1969, 1972, 1978). In fact, the proceedings of the Technical Sessions on Cane Sugar Refining Research (this issue) have several noteworthy contributions on this topic. All of the ion exchange processes proposed and currently in use are

based upon conventional, columnar and regenerable systems employing ion exchange resin beds and granules and utilizing chemical regenerants. Recent trends throughout the world have demanded that these systems be re-examined in terms of energy consumption, pollution, and capital investment. This paper describes a new phase of ion exchange technology that involves the use of powdered ion exchange resin formulations on a non-regenerable basis for clarifying and decolorizing cane sugar syrups thereby eliminating the need for regenerant chemicals.

THEORETICAL BASIS OF POWDERED ION EXCHANGE RESIN TECHNOLOGY

Powdered ion exchange resins and fine beads of ion exchange resins have been available for many years; however, their use has been limited primarily to laboratory chromatographic procedures and for some preparative processes in the fine chemical and pharmaceutical industries. The limited use of ion exchange resins having particle sizes finer than 100 mesh has been a result of excessive pressure drops and poor hydraulic performance. The use of smaller particles has been limited to the laboratory technique of high pressure liquid chromatography (HPLC). In the area of cane sugar refining, the use of ion exchange resins has been limited to relatively large particles (12-50 mesh) because of the high viscosity of the sugar syrups. This situation also prevails for the bone char and the granular activated carbon (GAC). Although powdered carbons are occasionally used, their handling problems are many.

Several years ago, the Graver Water Division of Ecodyne Corporation made a major breakthrough in water treatment by combining the unit operations of filtration and ion exchange into a single unit operation involving the use of powdered ion exchange resins on a disposable, non-regenerable basis. This technology has been used successfully by many steam-generated power plants (fossil and nuclear fuel), around the world for the polishing of condensates and for the removal of radioactive wastes. For these applications, Graver has developed a series of unique Powdex and Ecodex precoat filter formulations.

As a result of the success of Powdex and Ecodex in the power utility field, Graver has expanded their research and development activities in the development of other formulations for the treatment of drinking water, wastes, and varied industrial process streams. This Research and Development activity has resulted in the development of unique precoat formulations and processes for the removal of noxious compounds from water and wastes and for the clarification and decolorization of sugar syrups (beet, cane, and corn) and polyhydric alcohols (glycerine, sorbitol, etc.) (Blaine 1978).

The precoat technology developed by Graver and successfully applied to the polishing of condensate in the high pressure, steam-power generation plants was based upon the removal of

traces of soluble salts as well as insoluble corrosion products in a single unit operation. Heretofore, condensate polishing was practiced in two distinct operations; filtration of particulate corrosion products using inert precoat filters followed by deep beds of regenerable ion exchange resins to remove the soluble electrolytes. To combine the two objectives, Graver had to develop a unique precoat that would serve as both an effective filter and as an ion exchange demineralizer . Both of these operations had to be highly efficient in thin layers and with negligible pressure drops. To satisfy these requirements demanded the use of fine particles formulated in a manner that resisted excessive compaction and developed appropriate void volumes when the precoats were formed in thin layers.

The adsorptive or ion exchange operations require, in most instances, removal of greater than 95% of the soluble and particulate matter in the water or process stream to be treated. In fact, some situations require the removal of greater than 99% of the undesirable matter. The theories of adsorption and ion exchange indicate that the utilization of an adsorbent or an ion exchange resin column for a particular feed and leakage varies as the bed height of the column and temperature of the system and inversely as the flow rate, concentration, and particle size. These relationships are depicted in Figure 1. These relationships are primarily a result of the kinetics of the adsorption and ion exchange phenomena which are controlled by diffusional processes. It is mostinteresting to note that a fraction of an inch of a precoat layer of a powdered material can be as effective as several feet of a granular adsorbent or beads of an ion exchange resin. Further, a thin layer of a powdered precoat can operate much more effectively than deep beds of large particles at high linear flow rates. This conclusion follows from the fact that the length of the reaction zone decreases with decreasing particle size. The overall effect will vary depending upon the particular rate controlling mechanism which will be one of three diffusional processes - film diffusion, particle diffusion, or pore diffusion. Hence the effect of particle size on the reaction zone will be such that the length of the zone will increase directly as the diameter, the square of the diameter, or even between the two extremes since more than one diffusional mechanism may be controlling. As long as the concentration of the impurities soluble or particulate to be removed are relatively low, the thin layers or precoats are to be preferred over the deep beds of the granular material. In fact, in many cases, the precoats can be used more effectively and economically without regeneration or on a once-use, disposable basis. Of course, it follows that if the impurities to be removed are considerable, deep, regenerable beds are required in most cases.

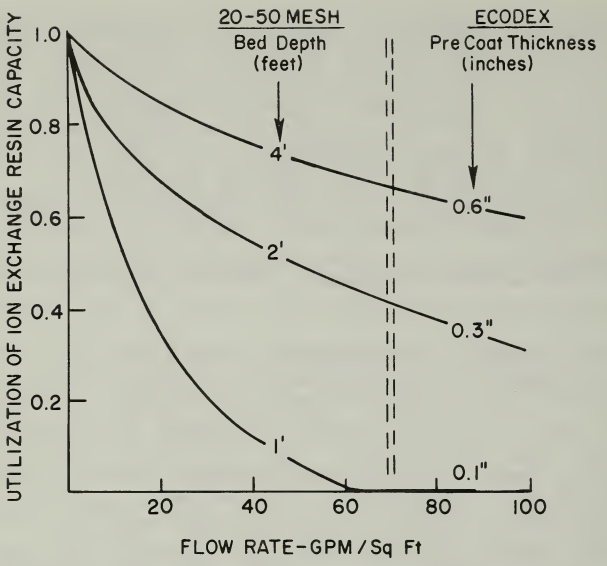

Figure 1.--Comparison of deep bed and powdered resin precoat performance.

NATURE AND PROPERTIES OF NEW PRECOAT FORMULATION, ECODEX S-1

The new precoat formulation is based upon the Ecodex technology developed by Graver for the treatment of condensates in the power utility field. As currently formulated for the power utilities, Ecodex is a homogeneous mixture of powdered ion exchange resins and fibrous material designed to provide capability for removing traces of soluble electrolytes and filtration of suspensoids and true colloids. The formulation is not a simple mixture of the basic ingredients. The ingredients have been interacted effectively so as to avoid segregation and migration, to minimize pressure drop and eliminate blinding of the filter elements, and so that the precoat can be formed without anyaddition of chemicals or prolonged mixing periods. The formulations can be used with and without body feeding and with all types of commercial precoat filters. The new formulation is based upon ion exchange resins tailored for the decolorization and clarification of sugars and polyhydric alcohols.

The Ecodex technology is much broader than indicated by the forementioned formulations. It can be extended to practically all types of ion exchange resins as well as other carbonaceous and inorganic adsorbents.

For food and potable water applications, the formulation has a composition and extractable level that comply with Food and Drug Administration Regulation # 121-1148 dated July 13, 1964.

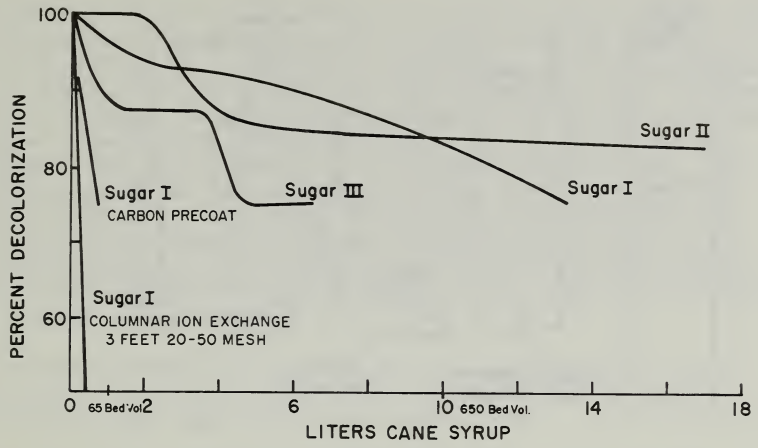

Figure 2.--Ecodex S-1 precoat performance for cane sugar decolorization. Precoat thickness, 1.9 cm; diameter, 3.2 cm; weight, 5.2 g (dry); volume, 15.3 cc; flow rate, 3.5 cc/min.

The Ecodex S-1 formulation is based upon the chloride form of a powdered, porous, strongly basic anion exchange resin derived from a styrene-divinylbenzene copolymer. This formulation has been designed specifically for the decolorization and clarification of sugar and polyhydric alcohol syrups. The effect of particle size on the decolorization capacity of anion exchange resins is quite dramatic because particle diffusion is a controlling factor and hence the length of the reaction zone varies directly as the square of the particle radius. Restated, the overall decolorization varies inversely as the square of the particle radius. If one compares the decolorization capacity of the Ecodex S-1 precoat formulation with the standard 16-50 mesh beads currently being used for the decolorization of sugar syrups, the precoat yields capacities ranging from 50-100 times that of the 20-50 mesh beads.

In most sugar refining operations, particularly in the cane sugar sector, decolorization is the major objective. The Ecodex S-1 development is quite timely because of its unusually high capacity for decolorizing sugar syrups and its ability to combine this property with clarification. Figure 2 summarizes the performance of Ecodex S-1 for decolorizing three North American cane sugar syrups. The data were obtained in the laboratory employing an apparatus, (Figure 3), that

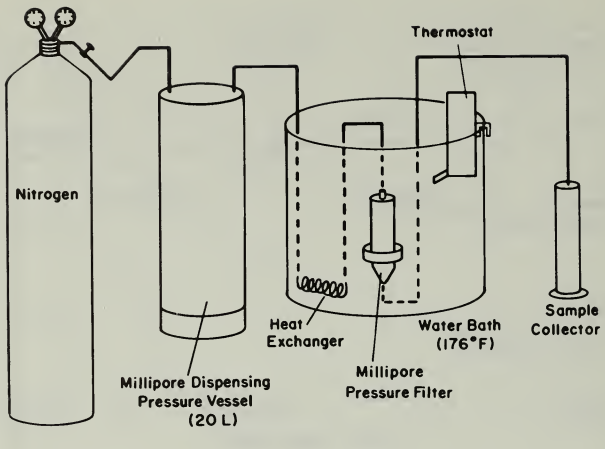

Figure 3.--Precoat filtration apparatus

simulates the dynamics of a commercial precoat filter. The variations are a result of the differences in the initial or pre-treated color values. A comparison is given using a typical carbonaceous adsorbent and a conventional ion exchange resin of normal-bead size. The data require no explanation.

As a result of this unique combination of properties, the use of Ecodex S-1 has the following three basic and noteworthy advantages:

1. Low Capital Investment
2. Reduces Energy Costs
3. Eliminates Chemical Pollution Problems

Although the conventional columnar, regenerable ion exchange systems exhibit these advantages over the use of bone char and granular activated carbon systems, the use of Ecodex S-1 exhibits these same and additional advantages over the conventional ion exchange resin systems. It is of interest to examine, in detail, the rationale for this statement.

Because of the extremely high capacity for decolorization, Ecodex S-1 can be used but once on a disposable, non-regenerable basis. Therefore, the need for regeneration facilities and the pollution problems created by the waste chemical regenerants are eliminated. The high capacity of the Ecodex S-1 precoat reduces the sweetening-on and sweetening-off dilution to a minimum thereby reducing the amount of water to be evaporated. The energy savings are considerable and alone justify the use of the Ecodex S-1.

Another advantage of the Ecodex S-1 precoat technique over the conventional, regenerable system is based upon the high affinity of the anion exchange resin decolorizers for the multitude of colorant species in the sugar syrup. Many of these colorants are so strongly adsorbed that they resist the regeneration procedure resulting in the fouling and poisoning of the ion exchange resin decolorizers over prolonged periods of use. As the poisoning and fouling continues from cycle to cycle, the effectiveness and efficiency of the anion exchange resin decreases with accompanying capacity and quality losses and increased energy and regeneration costs. This deterioration in performance commences after the first cycle. The use of Ecodex S-1 avoids this problem.

The minimal waste and sugar losses associated with the use of the Ecodex S-1 is virtually eliminated by recycling the spent precoat to the sugar defecation process.

In summary, the advantages of the Ecodex S-1 technique over the existing techniques for decolorizing sugar syrups are as follows:

1. Reduced capital costs,
2. Lowered space requirements,
3. Reduced sugar losses,
4. Reduced energy requirements,
5. Consistent sugar quality,
6. Excellent clarification, and
7. Elimination of chemical regenerants and accompanying waste problems.

With current concerns over pollution and energy throughout the sugar industry, the use of the Ecodex S-1 technique has considerable potential, particularly since it may be used with existing precoat filters already on hand in many plants. Variations of the Ecodex S-1 are available for polishing operations involving liquid sugars requiring the removal of tastes and odors.

EQUIPMENT

In the early development of Powdex and Ecodex technology, Graver designed and manufactured precoat equipment uniquely tailored for the polishing of condensates. This equipment can be used with the new Ecodex PAC and Ecodex S-1 precoat formulations for many applications. However, these precoats may also be used with practically all types of filters including leaf filters and filter presses. The precoats involving the Ecodex formulations may also be employed using the continuous or intermittent bodyfeed techniques. In all instances, the spent precoats may readily be discharged as a high solids waste pulp.

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THE USE OF A TWO BED (ACRYLIC AND STYRENIC) STRONG BASE ION EXCHANGE SYSTEM FOR THE DECOLORIZATION OF CANE SUGAR LIQUORS

William Fries and Robert W. Walker

Rohm and Haas Company

INTRODUCTION

The use of synthetic quaternary resins for the decolorization of sugar syrups dates from the early 1950's. In that era efforts were made to optimize these resins in the direction of lower crosslinking and higher moisture content in order to speed the diffusional rates of the large color bodies to the polymeric adsorption sites in the polymer backbone within the resins. However, this effort was limited by the physical instability of very high moisture, gelular resins. The backbone structure of these resins was a styrene/divinylbenzene copolymer with very small passageways (microporosity) dictated by the distance between the crosslinks. These types of resins are still being used in the treatment of very light color liquors after bone char to produce ultra-white sugar. Great care must be practiced to prevent high color levels from entering this resin--otherwise rapid fouling occurs.

In the 1960's a revolution in structure occurred in that copolymers could be made containing macroreticular pores. This allowed for the further incorporation of moisture with no loss in physical stability. The practical capacity of these resins for color was greatly enhanced which led to wide-spread commercial use of resins as polishing agents after bone char or granular carbon which increased the efficiency of carbon and lowered costs. In the 1970's, a third significant advance occurred with the use of acrylic quaternary resins. This allowed, for the first time, the possibility of an all ion exchange decolorization system in cane sugar refineries without the use of bone char or activated carbon.

The particular advantage offered by acrylic based resins was high decolorization efficiency coupled with the ability to efficiently remove adsorbed color from the resin with 10% brine solution. The selectivity and ultimate capacity of styrene

based resins for the color is higher, but the color is not as efficiently regenerated from the resin. However, the combination of an acrylic resin in the primary position to remove the dark colors (with efficient regeneration to prevent fouling) followed by a styrene based resin for polishing (to remove final color with less regeneration efficiency) proved ideal. Each resin was well suited for its specific function as the acrylic resin protects the styrene resin from fouling.

The mechanism of the color sorption is primarily adsorption with the resin's backbone interacting, not the ion exchange groups. This is indicated by following the balance of inorganic ions in the syrup both before and after the resin treatment. No net change occurs. It has been demonstrated that much of the color contains some aromatic character. This explains why color is more selectively held by the backbone of styrene based resin, that is because of ¶ - ¶ bond overlapping of the aromatic groups, while selectivity of the backbone of acrylic resins for sugar color is not as great, although sufficiently large to reduce color 50-80% in practical treatment. Because of this lessened selectivity for acrylic resins, the color adsorbed is very efficiently regenerated.

A significant number of refineries in South America and South Asia are presently using a system based on acrylic or a combination of acrylic and styrene resins, in some instances with over 10 years service. Primarily, their use has been with phosphatation streams (and in South America Talofloc-Taloflote clarification) followed by bone char. There are also refiners who are using a resin system directly after phosphatation without bone char. In this type of design the need for effective prefiltration such as a sand filter is required in the clarification procedure to eliminate insoluble material which may foul the resin system and cause excessive pressure drop in the resin beds (Cheong and Mussebah 1980).

A resin decolorization system is clearly subject to various syrup conditions which may affect performance. In response to these fluctuations, the resin operation conditions also can be varied to compensate. In an attempt to quantify these effects, this paper pulls together 10 years of laboratory decolorization experience.

DISCUSSION

Decolorization Studies

The parameters which have the most effect on the ability of ion exchange resins to remove sugar color are:

Uncontrolled	Typical Ranges
Color Level	100 - 4000 mau
Ash Level	300 - 3000 ppm

Controllable

Flow Rate	Related to size of columns	1-6 BV/hr
Throughput		3-110 BV/cycle
Temperature	Related to productivity	70-90°C
Brix		60-70
pH		7-8.5

Resin Related

Resin Type and Matrix (Gelular versus Macroreticular and Styrene versus Acrylic)

Resin Age

Regeneration Level or Type

The resins used in this study are all commercially available.

Amberlite IRA-401S - gelular quaternary resin based upon the copolymer of styrene and divinylbenzene

Amberlite IRA-900 - macroreticular quaternary resin based upon another styrene DVB copolymer

Amberlite IRA-458S - Gelular quaternary resin based upon a copolymer of methyl acrylate and divinylbenzene

Amberlite IRA-958S - macroreticular analogue of IRA-458S

The decolorization studies were performed in small columns. The resin beds were 0.5 to 4 inches in diameter and 18 inches high. The columns were thermostatically controlled with a water jacket and the syrups were introduced downflow at the prescribed flow rate. Approximately, one foot of void space was left at the top of these columns primarily for backwashing purposes. However, the entering syrup was allowed to accumulate into this void space above the resin bed for preheating purposes. The resin was held in place by a 70 mesh stainless screen. The syrup colors, both influent and effluent, were monitored by the ICUMSA method using a Talometer.

Laboratory work has encompassed studies with a variety of sugar source colors and ash levels. Results clearly show advantage of the two-bed over the single bed system. This information can be broadly correlated (Figure 1) with the total color exposed to the resin(s); this is defined as the

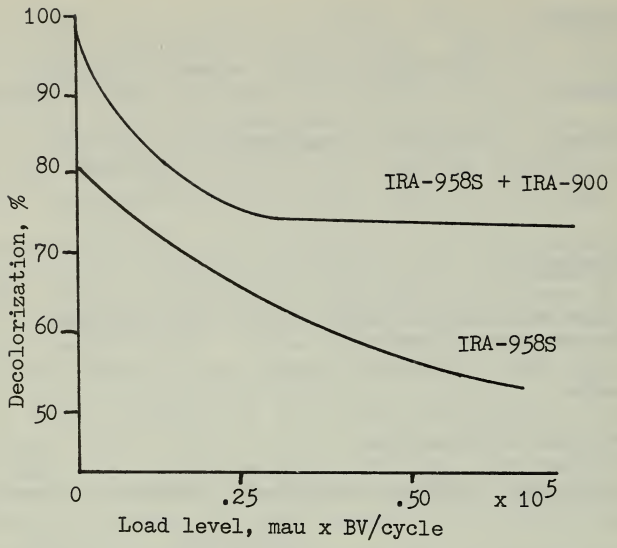

Figure 1.--Influence of the main variable effects of syrup color and cycle length upon decolorization.

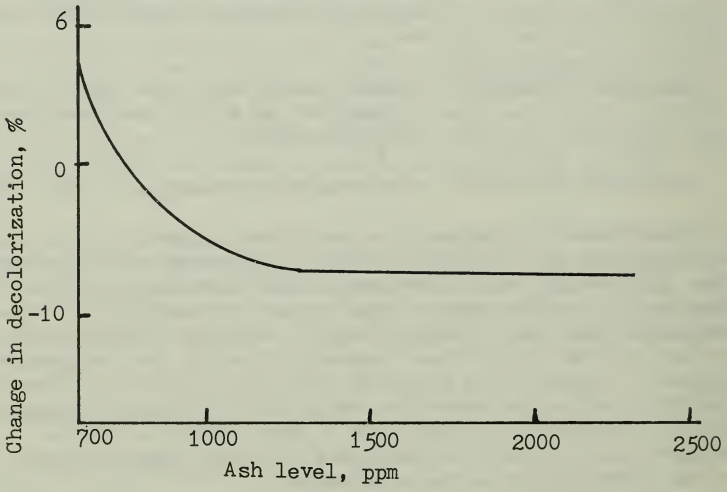

Figure 2.--Effect of ash level on the decolorization efficiency of IRA-958S.

influent color (mau) multiplied by the throughput per cycle (BV/cycle). Percentage decolorization is the output variable.

The effects of other variables on resin performance are important but of less significance. Further studies are needed to quantitatively define their influence. The relative magnitude and direction of these effects is given in table 1.

Table 1.--Secondary variable effects

Variable	Relative order of importance	Effect of increase in level of variables on decolorization performance
Syrup ash	1	Negative
Syrup pH	2	Negative
Syrup temperature	3	Negative
Syrup flowrate	4	Negative

Of these effects ash is the most significant. The effect of ash is shown (Figure 2). This figure is designed to be an adjustment to the information in Figure 1 for Amberlite IRA-958S. In general, these secondary effects are less important with the two bed rather than the one bed system.

One laboratory study in particular, lasting for over one year, emphasized the decolorization of refinery syrup completely without the use of bone char or any other adsorbent. Talofloc-Taloflote was used to aid phosphatation and a full flow filtration of the syrup was used. Several affiniated syrups were studied ranging in color from 1000-2000 mau. The clarified syrups entering the ion exchange resin beds ranged in color 260-460 mau. All the syrups were 60 brix. A two bed system composed of 70% Amberlite IRA-958S followed by 30% Amberlite IRA 401S was operated downflow with regeneration performed countercurrently upflow with 15 lb $NaCl/ft^3$ containing 0.2% NaOH. Over one hundred cycles were performed with the flow rate of the syrup through the resin and the syrup throughput per cycle varied. The computer model analysis of the results are depicted in Figure 3 and 4. The independent variables of volume of syrup treated per cycle (BV/cycle) and the color of the syrup influent to the resin system are related to the syrup color in the effluent from the resin system (Figure 3). Figure 4 gives the same data in a different form where the flow rate (BV/hour) is related to both throughput per cycle (BV/cycle) and the percentage of the influent color leaving the resin system. Clearly, ion exchange resins can consistently produce satisfactory syrup (<100 mau color) without the use of bone char.

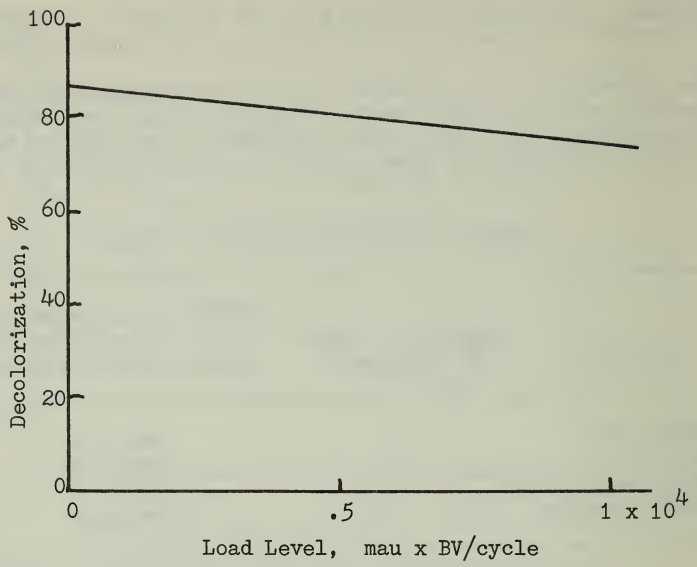

Figure 3.--Amberlite IRA-958S + IRA-401S with bone char. Computer model analysis of data. General correlation can be applied over flow rate range of 2-8 BV/hr.

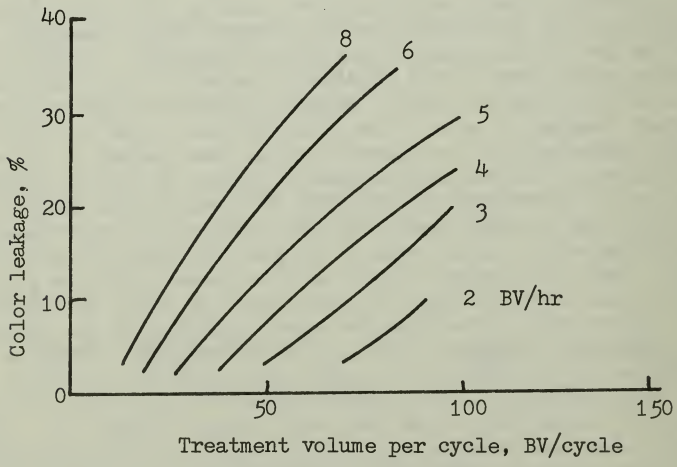

Figure 4.--Amberlite IRA-958S + IRA-401S decolorization without bone char. Computer model analysis of data. These correlations applicable over color range to resin bed of 260-460 mau.

Pressure Drop

The pressure drop of decolorization resins in packed beds treating high brix syrup was also studied. These results were obtained in a glass column one inch in diameter and up to 6 feet in height. Pure recrystallized cane sugar was used under the following conditions:

Syrup Brix	= 68°
Syrup Viscosity	= 18.4 centipoise
Temperature	= 70°C
Bed Height	= 4 foot

The results are shown in Figure 5 as a function of syrup flow rate. The macroreticular structure of Amberlite IRA-958S gives less pressure drop than either the gelular analogue, IRA-458S, or even the macroreticular styrene based resin, Amberlite IRA-900S. This is true even though Amberlite IRA-958S has the highest moisture content.

Regeneration

Sugar decolorization resins are regenerated after exhaustion with syrup color by passing brine (approximately 10% by weight) either co or concurrent to the direction of syrup flow (bed must be retained from expansion in countercurrent mode). During regeneration, the brine concentration rises slowly because of mixing of the heavier brine solution entering the top of a resin tank with the water already in the tank. At about an effluent concentration 4-5% NaCl at the tank bottom (about a 13.5 to 15.5 lb/ft^3 NaCl already in the column), the eluted color is at a maximum and diminishes rapidly in spite of further introduction of brine.

At least 13.5 pounds of pure NaCl (in a 10% brine form) per cubic of resin is required for an efficient downflow regeneration. This is clearly demonstrated in Figure 6 where the effect of brine regeneration level upon the subsequent decolorization efficiency of a two-bed resin system is given.

Commercial Use of Acrylic/Styrene Ion Exchange Systems

A simplified schematic of a refinery is given in Figure 7. The top is a refinery as presently practiced in which bone char is the integral decolorizing system with secondary, but important, roles played by the clarification and ion exchange resins. The bottom is a refinery in which ion exchange resins are the central and final point in decolorization. Bone char is eliminated. The resins are generally aided by a Talofloc-Taloflote modified phosphatation. However, direct treatment of carbonatation juice is possible also. The economics and ease of operation of the no bone char system are more favorable. Typical syrup quality before and after ion exchange resin

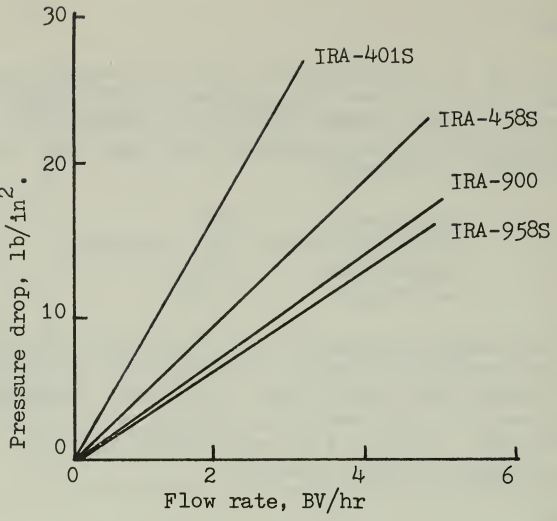

Figure 5.--Pressure drop.

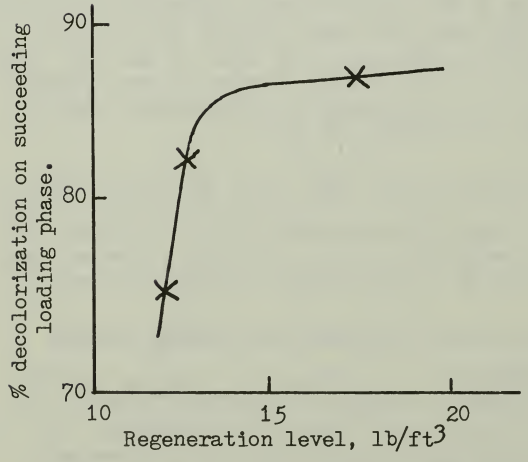

Figure 6.--Effect of regeneration level (NaCl) upon subsequent decolorization ability of IRA-958S + 401S system. Talofloc syrup. Color 359 mau. pH 8.0. Flow rate 4.5 BV/hr (total resin). Temperature 80°C.

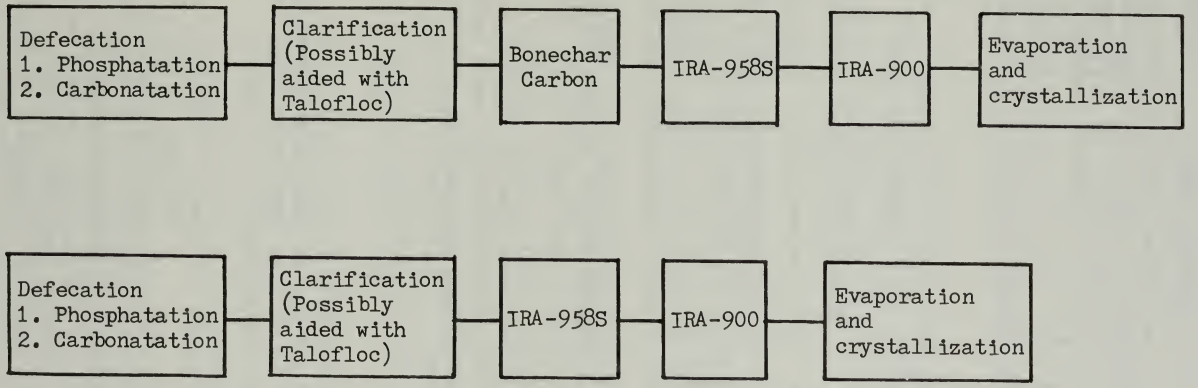

Figure 7.--Flow diagram of the clarification and decolorization section of a cane refinery.

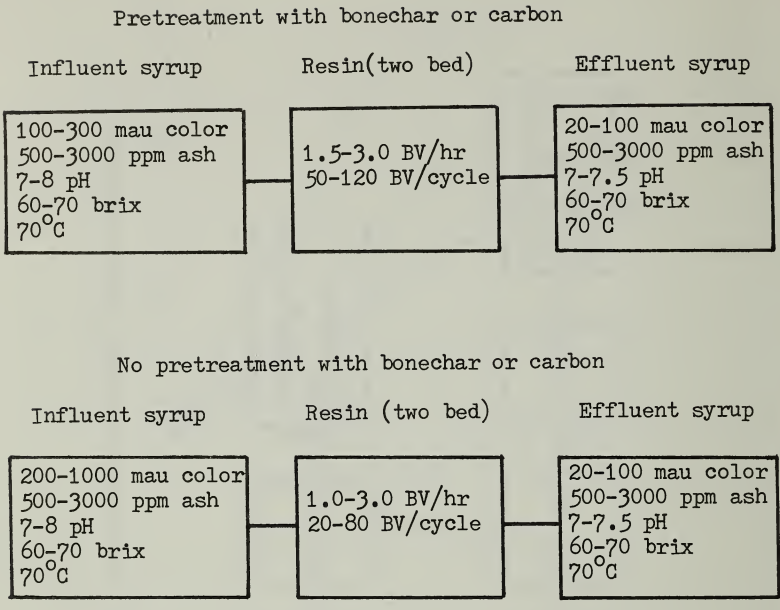

Figure 8.--Commercial conditions for ion exchange resin use.

treatment for both systems are shown in Figure 8. Generally, slower resin flow rates and shorter runs (more resin) must be used when treating the darker colored juices not pretreated with bone char.

REFERENCE

Cheong, Ong Ie, and Mussebah, H.
1980. 10 years experience with anion resins as gross decolorizer in cane sugar refining. Proc. Internat. Soc. Sugar Cane Technol. (in press).

DISCUSSION

R. RIFFER: Does your 958 resin have FDA approval?

R. W. WALKER: At this time 958 does not have FDA approval. But, we can give you a status report: We have verbally reviewed all of our findings including toxicity work with FDA. The reaction from FDA was most favorable. We have now officially filed a petition with FDA for their approval. We anticipate receiving approval by mid 1981.

R. S. PATTERSON: For the acrylic resin, what do you consider

the maximum safe temperature?

R. W. WALKER: These resins are also used in water treatment, where they are in the hydroxide form. Under these conditions we recommend a maximum of 35°C (95°F). In the chloride form, as they would be used in sugar decolorization, they have excellent stability in the 70 to 90°C (160 to 195°F) temperature range.

C. J. NOVOTNY (Industrial Filters): For the optimum regenerant level of 14 lb/cuft, do you use fresh brine in both resins?

R. W. WALKER: These studies were using fresh brine, at the level of 14 lb/cuft of each of the 2 resins.

C. J. NOVOTNY: Is the flow rate of 1 to 3 bed volumes per hour that for the volume of each resin or for the total of both?

R. W. WALKER: The figure is per volume of each resin.

H. R. DELANEY: In table 1 ash was the most important variable among temperature, pH, and flow rate. And then in figure 2 the effect of ash levels off. How do you explain that?

W. FRIES: Figure 1 is the main variable effects. Figure 2 is the secondary variables. Why it levels, I don't know. We see this happening quite often. That is why we drew the curve the way it was. Generally the inorganic anions compete for the adsorption sites.

H. W. DELANEY: Do you have any data on the constituents of the ash? We also found that there is competition and we found that specific anions and cations will effect it. The leveling off could be a function of a certain ash constituent.

W. FRIES: We do not have any data on specific constituents. This represents the summation of many different syrups, so I am sure it varies quite a lot.

C. C. CHOU: In your petition to FDA concerning the acrylic resin, did you specify the maximum temperature at which the resin was allowed to operate?

R. W. WALKER: All of our studies in support of FDA were done at 70°C, so we propose that be the operating temperature.

A COMPARISON OF THE STRUCTURE AND PROPERTIES OF BONE CHAR AND ION EXCHANGE RESINS FOR CANE SUGAR REFINING

Robert Kunin

Graver Water Division of Ecodyne Corporation

INTRODUCTION

This paper covers a period of four decades in which I was involved in research and development on the nature and behavior of both inorganic as well as organic adsorbents, ion exchangers, and catalysts. A considerable fraction of this period has been directed towards sugar refining. Although many of this group know me by my activities in the field of ion exchange resins, I doubt that many of you are aware of my activities on bone char. Since there are many representatives here from the sugar industry, I probably should also confess that my wife and I lost our sugar ration books when we were married in 1942. Since we were unable to obtain new ones during World War II, we learned how to drink coffee and tea without sugar.

Since the Cane Sugar Refining Research Project was originally known as the Bone Char Research Project, it is not necessary for the author to delve into the importance of bone char in cane sugar refining. A visit to a typical cane sugar refinery employing bone char would soon impress the visitor as to the importance of this refining aid, particularly with respect to the real estate required for the char house. The volume of the char units has been the envy of the ion exchange resin manufacturers for years.

STRUCTURE OF BONE CHAR

Since bone char has been employed almost universally for the refining of cane sugar, it is understandable that the proceedings of the Bone Char Research Project and the Cane Sugar Refining Research Project are replete with papers and discussions on the structure and adsorption mechanisms of bone char. At the 1959 Technical Session of the Bone Char Research Project in Montreal, I proposed a mechanism based upon some unpublished work I did in 1942-1944 while working as a chemist in the Chemical Research Division of the Dept. of Chem. Engr.

of the Tennessee Valley Authority (Wilson Dam, Alabama). In brief, in my 1959 paper, I proposed that the active ingredient of bone char was the calcium phosphate or more specifically, the hydroxyapatite structure. I further hypothesized that hydroxyapatite was an amphoteric, inorganic ion exchanger that could be represented by the following chemical structure:

$$Ca^{++}_{(8-10)}\ (H_3O^+)_{0-4}(PO_4)_6\ (OH)_2$$

As complicated as this structure may appear, it represents the hydroxyapatite structure generally represented as

$$Ca_{10}(PO_4)_6(OH)_2$$

According to the theory set forth by the author, up to 2 calcium ions and 2 hydroxide ions can be replaced or exchanged by other cations and anions on an equivalent basis according to the Law of Electroneutrality. This amphoteric ion exchange process can take place without any distortion or collapse of the basic hydroxyapatite structure. For example, fluoride ions, F^-, can exchange with the hydroxide ions, OH^-, of the hydroxyapatite forming fluorapatite which is isomorphous with hydroxyapatite both of which are indistinguishable from each other except by chemical analysis. Interestingly, the fluorapatite is less soluble than hydroxyapatite. This mechanism, by the way, has been used to remove fluoride from water and is responsible for the prevention of dental caries by the fluoridation water.

The exchange of the calcium ions with the hydronium ions (H_3O^+), hydrated hydrogen ions, H^+, can proceed to the extent of 4 H_3O^+ ions for 2 Ca^{++} ions forming a calcium deficient lattice without any collapse of the hydroxyapatite crystal structure. Other cations such as K^+ and Mg^{++} can exchange for the Ca^{++} and the H_3O^+ ions and it also follows that anions other than F^- ions can exchange for the OH^- ions. These include $SO_4^{=}$, Cl^-, and organic acids. The "regneration" of the amphtoric exchange capacity of the bone char is accomplished during the hot, sweetening-off process.

Although the inorganic, hydroxyapatite structure of the bone char is responsible for some of decolorizing activity, the carbon nucleus is also active as a decolorizing agent as well as a support for the porous structure. The relative functions of the carbon network and the inorganic hydroxyapatite structure became evident during the work on Synthad, a synthetic version of bone char originally developed at Mellon Institute and produced by Baugh and Sons.

ASH REMOVAL

In more recent years, the true value and function of bone char has become more apparent. Not only does the bone char remove

color from the cane sugar syrups, it may also remove a portion of the ash impurities. The technology surrounding the use of bone char has been developed to the point where it can be applied routinely and effectively without destroying any of the sucrose values through inversion. The structure of bone shar is such that it also is effective in removing haze and some invert sugar that is present in the cane sugar syrup that is to be refined. These functions of bone char are not surprising in view of the physical and chemical structure of bone char; however, the deashing function of the bone char, although of low capacity, is not generally realized under all conditions. In fact, the deashing capacity of the char is often "over-run" yielding effluents which are high in ash content.

REGENERATION

Of course, the above remarkable functions of bone char in sugar refining are not achieved without some payment. The capacity of the bone char to perform these functions is not very high and considerable investment in equipment is required for the furnace or kiln operation that is required for the regeneration or rejuvenation of the char. Large furnaces, extremely low rates, and large bone char units are required to realize the full capacity of the chars. Some of the same problems are encountered with granular carbons. These are serious limitations and have become more serious in recent years as expansions of plant facilities are considered. Of more importance are the energy considerations associated with bone char, not only the energy associated with the furnace operation but also those associated with syrup dilutions occuring during the sweetening-on and sweetening-off operations. With energy costs having increased from $0.50 to $5.00 per million BTU's since 1973, one can readily see why there is a realistic concern over the furnace costs as well as the costs for evaporating water introduced during sweetening-on and sweetening-off operations.

REPLACEMENT OF BONE CHAR

If one examines the bone char operation, an obvious point to consider is the possibility of devising other adsorbent systems that will perform the functions of bone char but will not require the furnaces or "retorts" for regeneration and perhaps will perform these functions more effectively with respect to capacity and degree of purification. If the systems are to be based upon ion exchange resins, they will have to satisfy the following conditions:

1. The system should decolorize and deash the cane sugar syrup following the defecation and clarification stage.
2. The ion exchange system should accomplish these functions at elevated temperatures without significantly increasing the invert sugar.

3. Regeneration of the ion exchange system should be relatively simple and economical.
4. The ion exchange resins should be quite stable and resistant to fouling.

In view of the considerable experience accumulated to date with cation exchange resins on the inversion of sugar and the stability and fouling of anion exchange resins employed in the deionization and decolorization of sugar liquors, the above requirements lead one to the following conclusions concerning the possible choice of an ion exchange resin system.

1. Sulfonic acid cation exchange resins cannot be used because of their high catalytic activity for inverting sucrose.
2. The cation exchange resin will have to be a weak acid cation exchanger such as a carboxylic acid cation exchange resin.
3. The carboxylic acid cation exchange resin will have to be used in a mixed bed unit since this ion exchange resin is still capable of inverting sucrose when used by itself due to the generation of ion exchanged acidity.
4. The anion exchange resin will probably have to be a porous weak base anion exchange resin, preferably possessing a tertiary amine structure.

These conclusions are based upon the facts that all cation exchangers in the hydrogen form (this is the form required for deashing) will invert sucrose at rates in excess of desirable limits if employed at the elevated temperatures being considered. The only hope of employing a cation exchange resin would be to employ the carboxylic acid type in a mixed bed resin system. The high temperature and regeneration requirements lead one to select the tertiary amine weak base anion exchange resin since the primary and secondary amine structures are unstable in the presence of invert sugar, some of which is always present. Finally, since both ion exchangers are weak electrolytes, equilibrium considerations dictate the use of a mixed bed unit containing Amberlite IRC-50 and Amberlite IRA-93. Amberlite IRC-50 is the cation exchanger and Amberlite IRA-93 is the anion exchanger.

OPERATION

The operational details for the use of the weak electrolyte mixed bed systems for refining cane syrups are described in Table 1. The performance of the ion exchange system employing this mixed bed is described in Table 2. Contained in this table are data for a fresh bone char column.

TABLE I

Details for Operation of Mixed Bed Ion Exchange System Using Amberlite IRA-93/Amberlite IRC-50 Resins

1. Ratio $\frac{\text{Amberlite IRA-93}}{\text{Amberlite IRC-50}} \quad \frac{4}{1}$

2. Operational flow rate = 0.25 gal./cu. ft./min.

3. Sequence of Monobed resin unit operation conducted at 60° C.
   a. Sweetening-on
   b. Exhaustion
   c. Sweetening-off
   d. Backwash to separate the two resins

4. Sequence of regeneration operation conducted at 50-60° C.
   a. Regeneration of Amberlite IRC-50 with HCl or H_2SO_4 at 150% theory
   b. Water rinse
   c. Rinse of Amberlite IRA-93 with acid-salt regeneration effluent from Amberlite IRC-50 or with a 4% N_aCl solution
   d. Rinse with 2 to 3 bed volumes of H_2O
   e. Regeneration of Amberlite IRA-93 with NaOH (or NH_3) at 150% theory
   f. Water rinse
   g. Remix of two resins

NOTE: The ratio of the ion exchange resin components of the mixed bed resin unit may vary between 3:1 and 4:1 depending on the quality of the clarified liquors being treated and the results desired.

TABLE 2

A Comparison of Processing Clarified Cane Sugar Liquors by Bone Char and an Ion Exchange Resin Mixed Bed System

Type of Treatment	Clarified Sugar Syrup (Before Ion Exchange Treatment	Bone Char[2]	Amberlite IRC-50/ Amberlite IRA-93
Volume processed (BV)		3	13
pH	6.65	7.10	7.15
Sp. Resist.;[1] ohm-cm.	6,600	8,000	200,000
Decoloration (%)	----	82	97
Na; ppm as $CaCO_3$	52	52	6
K; ppm as $CaCO_3$	122	105	4
Ca; ppm as $CaCO_3$	225	122	2
Mg; ppm as $CaCO_3$	37	28	4
Total Cations	436	307	16

[1]Specific resistance measured for 15 Brix solution after dilution of the 60 Brix liquors with D.I. water

[2]Bone Char operated at 0.1 gal./cu.ft./min. or less

[3]Ion Exchange resins operated at 0.25 gal./cu.ft./min.

The data of Table 2 clearly indicates that the Mixed bed ion exchange resin system satisfied the basic requirements set forth in the above discussion and the data also clearly illustrates the superiority of the weak electrolyte resin system over bone char for both deashing and decolorization. The weak electrolyte ion exchange resins employed in mixed bed resin unit have been found to possess excellent physical and chemical stabilities for this application and, therefore, stability of these ion exchange resins should not be a major factor in the economics of this technique. With respect to sucrose inversion, the data indicate that the mixed bed system is suitable for this application. Operated at about 60·C, sucrose inversion using the mixed bed resin system is about the same as found for bone char operated at 82°C.

The capacity of the column of mixed bed resins is limited by the capacity of the weak base anion exchange resin, based on pH and specific resistance data. Although the anion exchange resin still is capable of decolorizing more feed than actually processed, the runs were terminated because of the drop in pH which becomes a limiting factor as to when a particular cycle must be ended to prevent excessive formation of invert. Were the aim

of the treatment primarily to decolorize the clarified juice, the proportion of anion to cation component could be further increased at the expense of sacrificing some deashing.

Prior to regeneration, the separation of the resin components of the ion exchange mixed bed resin system can be readily accomplished using relatively low flow rates and a minimum of backwash water. Time required to achieve good separation is short and hydraulic expansion required to achieve good separation is not extensive

DECOLORIZATION WITHOUT DEASHING

For the manufacture of crystalline sucrose from normal raw cane sugar that has been properly affinated and defecated, deashing of the syrup is questionable, particularly for the better than average raw sugars. In recent years, it has become more and more apparent that the major function of the bone char is that of decolorization. As a result, we now find anion exchange resins gradually replacing the bone char and granular active carbons. The deashing and polishing decolorization operation is now reserved for the liquid syrup production using a portion of the liquor decolorized by anion exchange resin operation. Here, we must compare the mixed bed based upon the strongly basic anion exchange resin and the weakly acidic cation exchange resin and that based upon the weakly basic anion exchange resin and the same anion exchange resin. The basic differences are as follows:

1. The mixed bed based upon the strongly basic anion exchange resin must be operated below 40°C whereas the other mixed bed can be operated at 60°C or even as high as 80°C.

2. The weakly basic anion exchange resin does not foul or poison nearly as readily as the strongly basic anion exchange resin.

ECONOMIC CONSIDERATIONS

It would be beyond the scope of this study to make any concrete conclusions as to the overall economic value of the weak electrolyte mixed bed resin system as a possible substitute for the bone char or granular carbon operation for refining cane sugar syrups since larger scale tests are, of course required; however, since one can operate the mixed bed resin unit at flow rates considerably greater than those employed for bone char, and since the furnace operations are eliminated, the capital costs for the ion exchange operation involving mixed bed should be considerably less than a comparable bone char operation.

It is also of interest to consider this study in the light of the progress previously made in the use of ion exchange resins for refining cane sugar. Ion exchange resins are now employed economically for the decolorization and deionization of cane sugar syrups following either a carbon or bone char pretreatment. The new mixed bed resin system is merely a continuation of this progress. By merely employing ion exchange resins that have already been used extensively for water treatment and other sugar milling and refining operations in mixed bed equipment, and also successfully used for cane sugar decolorization and liquid cane syrup production, it appears that one may be able to extend the use of ion exchange resins in cane sugar refining augmenting or eliminating the use of carbons and bone char.

Any savings that may be achieved with regard to regenerant costs for the ion exchange resins will render the process more attractive from an economical viewpoint. It has been possible to obtain complete regeneration of the weak electrolyte ion exchangers with HCl or H_2SO_4 for the weak cation exchange resins and NaOH for the Amberlite IRA-93 at regeneration levels approaching 150 percent of theoretical exchange capacity of the ion exchange resins. Theory suggests that further studies aimed toward reducing the regeneration levels are warranted. The use of NH_4OH for the Amberlite IRA-93 and SO_2 for the weak cation exchangers might be investigated. Should NH_4OH be found effective, NH_3 could be recovered from the waste regenerant with an equivalent amount of lime and reused for the subsequent regeneration of the Amberlite IRA-93. This technique is used universally in the manufacture of soda ash and has been used to advantage by the beet sugar industry in France. In the case of SO_2, the gas could be scrubbed out of flue gases resulting from the burning of sulfur-rich coals or obtained directly from the burning of sulfur. Burning of sulfur to produce SO_2 has been practiced by sugar beet refiners who practice sulfiation in their sugar beet refining operations. Finally, depending on the ultimate purity of the cane sugar desired, several modes of operation are possible as is evident from the data presented for the mixed bed resin system employing Amberlite IRC-50/Amberlite IRA-93 ion exchange resins.

Several tests performed on the composite of the treated syrups indicated that the mixed bed resin unit was capable of removing traces of haze present in the feed and that no odor was introduced into the final product. Boiling tests on the final product indicated that the mixed bed resin column removed most of the color precursors.

DISCUSSION

F. G. CARPENTER (Southern Regional Lab.): Your observation that carbon is not important in bone char is supported by observations made from time to time. Many years ago at Yonkers, something went wrong in their kiln regenerating bone char and all of the carbon was burned off. They had white bone char. But, it still decolorized sugar. However, the capacity for color was very low. It does show, however, that carbon is not the only seat of decolorization.

In regard to tricalcium phosphate, I agree with you completely that the calcium phosphate precipitate in raw sugar clarification, the precipitate in phosphate clarifiers, the mineral part of bone char, and even the "tricalcium phosphate" sometimes promoted as an anti-caking agent in powdered sugars is in fact not tricalcium phosphate. All of these materials have the x-ray diffraction pattern of hydroxyapatite, but as you pointed out, the stoichiometry, that is, the calcium to phosphate ratio is variable and may sometimes be close to that of tricalcium phosphate. I believe that the best explanation is that a rapid precipitation, such as in clarifiers, leads to an amorphous calcium phosphate with little or no crystal structure discernable by x-rays. Very rapidly, a solid phase rearrangement occurs producing crystallinity in the form of hydroxyapatite (whose Ca/P ratio is greater than that of tricalcium phosphate) and octacalcium phosphate (whose Ca/P ratio is less than that of tricalcium phosphate). These two well defined substances have crystal structures so nearly the same that x-ray diffraction patterns are almost indistinguishable, and also, most important, they can form intercrystalline layers. That is, a layer one or more unit cells thick of hydroxyapatite, a layer of octacalcium phosphate, a layer of hydroxyapatite, etc. This model explains all the observed facts and is another example of intercrystalline layers which was spoken of yesterday in relation to incorporation of dextran into sucrose.

R. KUNIN: I bow to Dr. Carpenter's more refined theory involving octacalcium phosphate. However, I feel that the solid solution concept of the behavior of hydroxyapatite also satisfies all the data. With respect to the white bone char, it is not possible that it was dead burned.

A MODEL VACUUM PAN: CRYSTALLIZATION STUDIES OF OCCLUSIONS

James A. Devereux

Cane Sugar Refining Research Project, Inc.

INTRODUCTION

Until recently, sugar boiling was considered an artistic talent requiring years of apprenticeship under a master sugar cooker. The demand for refined sugar grew, and so methods for the automation of sugar crystallization became necessary. Better and better instrumation for vacuum pans, and research done by such people as Holven and Gillette have made sugar crystallization more of a science than an art.

The Cane Sugar Refining Research Project, Inc. has conducted many studies on minor constituents in cane sugars. The behavior of minor constituents during crystallization became of interest: the distribution of known colorant compounds between crystal and liquor will show if certain compounds are selectively included in the crystal. Those compounds that do go into the crystal are the compounds (colorant and color precursor) that should be removed before the liquor goes to the vacuum pan.

To accomplish these studies, it was necessary to build a model vacuum pan. Requirements for the pan included adjustable pressure and temperature controls and measurement devices, a circulation mechanism and provision for addition of solid or liquid compounds.

The goal was to construct an apparatus that could produce reproducible yields, i.e., similar percentage of crystals, of similar size, from different boilings under similar conditions. Such an apparatus would be suitable for studying the distribution of an added non-sucrose component between crystal and syrup, to determine if some compounds were occluded in the crystal more than others.

SUCROSE CRYSTALLIZATION: ADAPTATIONS OF REFINERY PRACTICE FOR LABORATORY MODEL

Sugar crystallization is carried out in four steps. (1) Sugar syrup is boiled under vacuum until enough water has evaporated away that supersaturation occurs. (2) When a certain degree of supersaturation is reached, the pan is seeded with very fine sugar crystals to induce crystallization in the supersaturated solution. (3) The crystals are allowed to grow until they reach a certain size. (4) The syrup is centrifuged away from the sugar crystals. A more detailed description of these steps follows.

Step 1

When sucrose (table sugar) is subjected to excessive heat it will decompose into glucose and fructose and subsequently to organic acids and colorant compounds. To avoid this decomposition, sugar syrup is boiled under a vacuum so that a lower boiling point is achieved.

As water is boiled away, the concentration of the syrup is increased, thereby raising the temperature at which the syrup is boiling. Duhring's law states that if the temperature of one substance is plotted against the temperature at which another similar substance has the same vapor pressure, the

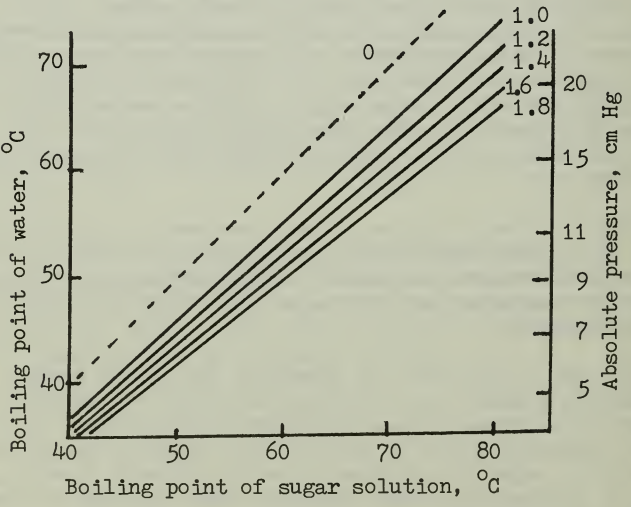

Figure 1.--Boiling point, vapor pressure and supersaturation of sugar solutions.

graph will give a straight line. A graph of boiling point of an aqueous sugar syrup versus the boiling point of water at the same pressure gives a straight line. From this linear relationship, it was possible to determine the degree of supersaturation by the boiling point of the syrup. The supersaturation of the solution is defined as:

$$\frac{C_{sol}}{C_{sat}} = \frac{\text{conc. of solution at some temp.}}{\text{conc. of saturated soln. at same temp.}} = SS.$$

The boiling point rise (BPR) of a sugar solution is defined as:

$$BPR = K\, C_{sol}\ , \quad \text{where K is the constant.}$$

Therefore,

$$SS = \frac{1/K\ BPR_{sol}}{1/K\ BPR_{sat\ sol}} = \frac{BPR_{sol}}{BPR_{sat\ sol}}\ .$$

Much work has been done to determine when saturation has been reached in a vacuum pan. The fact is that the saturation boiling point at a particular pressure is unique to each vacuum pan. Because of different geometric configurations among vacuum pans, temperature gradients will be different from pan to pan. As it is the temperature that ultimately determines the solubility, if there is a temperature gradient in the pan, then there is also a saturation gradient. It is the average of all these different degrees of saturation that is the real degree of saturation for the pan. The different saturation gradients for each pan make it necessary to determine each pan's own unique saturation point for a particular pressure. The saturation point will vary even if the level of massecuite is varied in the pan.

To determine the saturation boiling point at a particular pressure, a batch of massecuite with an excess of sugar crystals must be boiled under reflux at the same conditions that will be used in actual crystallizations until a constant boiling temperature is obtained. When a constant boiling temperature is obtained, the sugar and water in the pan have reached an equilibrium concentration. Since the solution is boiled under reflux and no water can escape, this equilibrium concentration is the saturation concentration for that pan at that pressure. The boiling point is the variable that can be measured and recorded to define the saturation point at that pressure in that pan.

Step 2

When the desired degree of supersaturation is reached, the vacuum pan is "seeded" with very fine sugar crystals. In theory, if the pan is seeded at a low enough degree of super-

saturation, the only crystals that will grow as the water boils off are the sugar crystals that are added as seed. The saturation gradients in the pan make it difficult to avoid spontaneous nucleation. In the industry this is sometimes desirable. Therefore, the pan is allowed to reach a high enough degree of average supersaturation to insure that spontaneous nucleation will take place on a large scale. If spontaneous nucleation is not desired, the the usual step in industry is to raise the temperature inside the pan enough to destroy these smaller crystals that formed spontaneously. After seeding takes place, the crystals are allowed to grow for a few minutes. Then the pressure is raised in the pan, which raises the temperature, which raises the solubility of sugar to below saturation. The crystals that formed spontaneously, which are much smaller than the crystals that were used to seed the pan, dissolve. The large crystals are strong enough to withstand the path back to saturation at the elevated temperature.

In the pan in this project, the pressure was kept constant throughout the entire boiling process so a method other than pressure variation had to be employed to solve the problem of spontaneous nucleation. A small amount of hot water was added to the pan soon after seeding. This process is commonly called "giving the pan a drink". The water brings the pan down to just below supersaturation; however, the water is heated in order not to lower the temperature of the pot.

Step 3

Determining saturation and avoiding spontaneous nucleation are the most crucial steps of the crystallization process. The next important phase is the adding of syrup to the pan to grow the crystals. The crystals will only grow in a supersaturated solution. In order to grow the crystals to the desired size, syrup is added to the pan to supply more sugar to grow the crystals. In theory, it should be possible just to evaporate all the water in the pan originally and grow the crystals, but in practice, the crystals in the pan in the early stages of crystallization are usually too small to absorb all the sugar left behind by the water as it boils off unless the water is boiled off very slowly. The massecuite will move into a higher level of supersaturation and spontaneous nucleation will occur, so that the massecuite will become too thick and conglomeration of the crystals will take place. In the pan in this project, the syrup was added at a rate to keep the temperature in the pan constant.

The amount of syrup added in this work was the same amount as was originally in the pan before boiling started. After all the syrup was added, the pan was allowed to boil down until the desired crystal size was reached. Boiling down at this point can be done safely because the crystals are large enough to absorb the sugar as fast as the water is evaporated. A

slight rise in boiling point may be observed as the boiling down occurs. It is the consensus of this research group that the rise in boiling point is due to the increase in pressure on the water throughout the pan because of the sugar crystals in the pan.

Step 4

After the boiling is finished and the vacuum broken, the massecuite is removed from the pan and the syrup centrifuged away from the crystals.

EXPERIMENTAL WORK

Initial Attempts

The first apparatus used included a water aspirator as a source of vacuum and a hot water bath heated by a heating plate to boil the sugar. The sugar syrup was placed in a 1000-ml round bottom flask and rotated in the water bath. It was impossible to seed this pan or add syrup. The results were just large conglomerates of very fine sugar crystals.

The next apparatus used a flat bottom flask placed directly on the heating plate. A magnetic stirrer was used to increase circulation and attempt to reduce conglomeration. A water aspirator was again used as the source of vacuum. A vacuum gauge with divisions of 1 inch of mercury and a needle valve to control vacuum were added. Again there was no way to seed or add syrup to the pan. As the syrup boiled and got more viscous, the magnetic stirrer became ineffective and the results were the same as the first time.

Construction of Working Model

A four-liter reaction kettle (Corning) was used as a pan, with a glass condenser with circulating cold water, to which was attached a 1000 round bottom flask to hold the condensate. The top of the reaction kettle has four ground-glass fittings, and is to be replaced by a top with four ground-glass fittings plus a one-inch hole in the center for the stirrer. The other apertures are for temperature and pressure controls, and addition of syrup or hot water. The reaction kettle was set in a thermostated glass hot water bath (Sargent Welch Thermonitor Mod. ST, plus 750 w immersion heater with voltage control.)

A separate index pan connected to the same vacuum pump and vacuum regulator as the vacuum pan was set up. The index pan was used to get the boiling point of water at the same pressure as in the vacuum pan. Another use was to calibrate the thermocouple recorder at the beginning of each day.

Stirring was accomplished by a 1/15 HP variable speed stirrer (General Electric). A plexiglass top will be constructed for the water bath with a hole the diameter of the vacuum pan cut in it.

A glass funnel with a filter to catch the sugar crystals was used in place of a proof stick. A vacuum hose that bypasses the pressure regulator is connected to the filter side of the funnel. A stopcock is inserted in the hose before the funnel. The other end of the funnel has a rubber stopper in it with a vacuum hose through it. This vacuum hose is connected to a brass tee. Connected to one end of the tee is a short vacuum hose with a pressure release valve in it. The other end of the tee leads through a stopcock into the massecuite in the pan. To get a sample out of the pan, both stopcocks are opened. The vacuum in the line will be much greater than that in the pan because the line bypasses the pressure regulator. A sample will be sucked into the funnel where it is trapped by the filter. Both stopcocks are turned off, and the pressure release valve opened.

To control the vacuum in the system a Cartesian manostat (Emil Greiner) is used. A mercury manometer reading to 0.1 mm, with a tube leading directly into the vacuum pan is used to measure the vacuum. Between the vacuum pan and the Cartesian manostat is a vacuum gauge with divisions of 1 inch of mercury. A vacuum pump (Precision Scientific Co., Model 150) is used to draw the vacuum.

To measure the temperature in the vacuum pan, a thermocouple (Chromel-Alumel) connected to a strip chart recorder (Sargent-Welsh No 310) was used. Because the recorder only measured the difference in potential in the thermocouple, it had to be calibrated to be used as a temperature measuring device. The calibration procedure is as follows:

1. The water in the index pan is brought to a boil under a vacuum, with temperature read by a glass thermometer with 0.1 ^{o}C divisions.

2. The temperature of the other end of the thermocouple, which is taped to the end of a thermometer in a semi-insulated styrofoam cube, is recorded. This end of the thermocouple was connected to the recorder by copper wire.

3. The paper on the recorder is divided into 250 lines. When the above two temperatures are recorded, record the line number on the recorder. Because the boiling point temperature is constant and the other end of the thermocouple is insulated, the line on the recorder should be straight.

4. The above procedure is repeated several (at least 5) times at various different boiling points in the index pan with varied pressures.

5. When the data were gathered, the difference in temperature of the two ends of the thermocouple was plotted versus the line number on the recorder. This step was done on a computer and put to a least squares fit. The slope of the line is the number of lines per degree centigrade.

The recorder is set daily so that line 240 always corresponds to the same temperature, by boiling the water in the index pan under vacuum before using the pan. The boiling point of the water and the temperature of the other end of the thermocouple are recorded, and and the recorder is set to line 240.

RESULTS AND CONCLUSIONS

The model pan as described here was used succesfully to boil white sugar, using a standard high grade white refined sugar as starting material, with a yield reproducible to ± 1 %, temperature conditions reproducible to ± 0.1 ^{o}C, and pressure conditions reproducible to ± 0.1 mm Hg.

The addition of ferulic acid, a known colorant precursor that comes from the sugarcane plant, at levels of 0.05 % and 0.1 % on solids, showed a reprodicible distribution between crystal and syrup in a ratio of 1:10. Other compounds, including vanillin, are being studied to see which, if any, enter the sugar crystal in a ratio of greater than 10 %.

ACKNOWLEDGEMENTS

At this point I would like to thank my coworkers in the Cane Sugar Refining Research group: Dr. Margaret Clarke, Dr. Frank Carpenter, Mary An Godshall and Earl Roberts. Without their help and great cooperation this project would never have been completed.

I also want to thank the engineering staff of Colonial Sugars, Gramercy, LA, Peter Petri of Audubon Sugar Institute, LSU, and Dr. Wilson Nicol of Tate and Lyle, Ltd., England, for their helpful advice and instructive discussions.

DISCUSSION

H. R. DELANEY: What were you using for seed?

J. A. DEVEREUX: We used as seed, finely milled fondant sugar suspended in ethyl alcohol.

H. R. DELANEY: What yield did you obtain?

J. A. DEVEREUX: The usual yield was about 50%.

H. R. DELANEY: In the centrifuging, how did you apply wash water to get reproducible results?

J. A. DEVEREUX: We would like to say our results were completely reproducible. The wash was deionized water applied with a squeeze-type wash bottle. We did not wash very much.

M. A. CLARKE: The washing procedure is not yet entirely systematized.

A. VANHOOK: Is vanillin a known color precursor and a known constituent in sugar?

J. A. DEVEREUX: Yes, our group found vanillin in sugar some years ago. It degenerates in boiling to give a yellowish color.

Symposium.--Experiences in decolorization alternatives

C AND H EXPERIENCES

Stuart Patterson

California and Hawaiian Sugar Company

As my part of the symposium I want to review our experience at C and H with bone char and granular carbon and experimental work with resin as well as to cover some miscellaneous aspects of decolorization.

At C and H we still rely on bone char as our primary decolorizing agent. We have 83 char filters each of 1600 cu.ft. capacity, divided into 3 Houses, two of which are regenerated by conventional retort kilns and the other House char is regenerated by a Herreshoff kiln. We also have 8 granular carbon filters of equal size (1600 cu.ft.),four of which have been in since 1960 and the other four were put into operation in 1974.

The bone char filters each handle Clarified Raw Liquor and intermediate, low purity materials for making our Soft Sugar. One change we have made here in the last two years is that where we had been just sending low purity material to our poorest grade char, we now send Clarified Raw Liquor for 30 to 40 hours, then the low purity material. Even though this char is heavy, low in carbon and finer in particle size, it can still do a good decolorizing job for a limited time because it has more surface area.

The No. 1 House char is sweetened off in place but then sent to a continuous de-ashing column and then to dewatering belts before going to the Herreshoff kiln. For our No. 2 and No. 3 House char we have been in and out of warm water washing over the past several years but we are now using warm water (70°C) washing because of the energy savings, although still finishing the wash cycle with hot water (90°C). Recently we have been running a modified battery sweetening off process in the char filters to conserve sweetwater and hence energy. To minimize inversion over our four day shut-downs we increase the pH of Clarified Raw Liquor onto char for the last 12 hours of shutdown day.

The granular carbon filters are treating a dark fraction of our No. 1 Liquor that is too dark to send to the pan floor and produce a No. 1 Liquor of acceptable color. The carbon filters have long cycles on this fairly light load, averaging about 35 days on this dark No. 1 Liquor before sweetening off. The carbon is regenerated in a 54" diameter, 6 hearth Herreshoff kiln. Again we increase the pH of liquor to carbon going into shut-down.

Not directly related to decolorization but a necessary part of char house activities is the necessity to satisfy EPA requirements with respect to the quality of air and water streams emanating from the char house. Over the past several years this has taken a good deal of time, effort, and capital to install wet and dry dust collectors to trap char and carbon dust and to install a primary waste station to collect settleable solids including char and carbon fines and a secondary waste station to take care of BOD coming primarily from the char house.

With respect to decolorization by resins we have tested resins at C and H probably every 10 years for the past 40 years. Each time, they did not provide sufficient economic justification to proceed with installation of resin columns. However in our last intensive study which has been going on in the past few years things have changed and we now are seriously proposing the use of decolorizing resins to do the major part of decolorization for our white sugar. The big thing that changed of course is the cost of energy which in the past 10 years has increased by a factor of about 10. When you substitute regeneration of resin by salt solution for thermal regeneration of bone char you obviously achieve substantial savings in energy.

In our proposed use of resins for decolorizing Clarified Raw Liquor we will be sending the liquor through the resin columns first then through bone char. This is the reverse to what most refiners who are using resins do. However with the improved quality of raw sugar that we are getting from the Hawaiian Islands and with the 25 - 35% color removal we are getting on our flotation clarifiers, our Clarified Raw Liquor is usually in the range of 700 - 850 1000a$^{*}_{420}$ color units and our testing program has shown that the resin can do a good job. At present we are not pressure filtering the Clarified Raw Liquor to char but included in the overall resin project are funds to activate some pressure filters we have so we will be pressure filtering the liquor to the resin columns. We plan to have 8 resin columns divided into four sets of 2 columns each and at any one time three sets of columns will be handling all our Clarified Raw Liquor flow while the fourth set is being regenerated. The resin in all the columns will be the strong base anion resin. We will regenerate the resin with alkaline brine solution because we have found the alkaline brine does a better job of removing the color from the resin than acidic or neutral brine. We believe most of the colorants are adsorbed on the resin

matrix rather than being removed by ion exchange. After sweetening off the resin columns the rinse water, backwash water and some of the spent regenerant brine will be sent to our BOD plant for treatment because of the sugar and organic colorant content. Then the rest of the regenerant, outside of a recycle portion, and the rinse waters, will be sent to the Carquinez Straits along with our condenser water effluent.

The move to resins as a major supplement to bone char for our white sugar is a change for our refinery but many refineries are using decolorizing resins and some are using de-ashing resins. What's different in our case is that we will be using the resin columns before char where other American refineries use the resin after char or carbon. In South Africa, Australia, Brazil and Japan some refineries are now using just resin without bone char or carbon so we are not exactly blazing a trail in refining practice. In some of the countries the acrylic based resins can be used and these seem to complement the styrene based resins, not tending to foul as readily and regenerating easier than the styrene based resins. When the acrylic based resins are approved by the FDA we would expect to use them in the first column and the styrene based resin in the second column of the set.

Also, on the subject of resins, Dr. Kunin is presenting a paper on the use of powdered ion exchange resins for decolorization of sugar liquors. A first reaction here is that this would seem to be a step backward because where powdered carbon used to be used in some refineries, in most cases this has now been displaced by granular carbon. However things change and since the powdered resin doesn't need to be regenerated and since it makes less sweetwater the technology needs to be evaluated to determine the effect on the bottom line economics.

Our panel is primarily discussing decolorization by bone char, carbon and resin or combinations of these adsorbents. However color removal is also obtained in other ways and in some of these, changes are taking place. Let's look at some of these other ways.

1. RAW SUGAR OPERATIONS

Let's look briefly first at raw sugar operations. I know this group is made up of refiners but we know that our refining operation and decolorization is dependent to a major extent on the quality of the raw sugar. In the case of C and H we are owned by the raw sugar producers in the Islands so it is quite often that a decision is needed on whether money should be spent to improve the quality of the raw sugar or to make changes in the refinery to take care of different quality levels. Recently in the Islands steps have been taken to improve the quality of the raw sugar, particularly with respect

to a higher pol raw with lower color. This has significantly improved our refinery operations.

A process that used to be practiced at raw sugar factories in some areas of the world was carbonation and I would be interested in knowing if anyone in the audience knows whether it is still in use.

A more recent development is the Talodura process that Tate & Lyle has introduced for decolorization and improvement of evaporator syrup at some raw sugar factories around the world. This process involves the addition of phosphoric acid and lime to the evaporator syrup, aeration, then addition of Talodura - a polyacrylamide flotation agent and then to a flotation clarifier.

Some raw sugar factories, particularly in South Africa, are producing a Very High Pol (VHP) raw sugar, usually over 99.3 polarization. This VHP raw sugar does not have to go through an Affination process so a major process step is eliminated.

2. AFFINATION STATION

We don't think of an Affination step as a decolorizing operation but we make a major improvement in the color of the liquor we are going to handle by putting the sugar through the Affination Station. Color of the whole raw sugar can be 2500 and up, while the washed raw sugar in our case is usually less than 1,000. Our only changes at the Affination Station affecting decolorization were the addition of frequency converters to increase the speed of the centrifugals and produce a better colored washed raw and computer control to give us more consistent operation.

3. PHOSPHATATION OR CARBONATION

Most refineries use either phosphatation or carbonation. For those refineries using phosphatation some use relatively small amounts of phosphoric acid and send the treated liquor to pressure filters: others use higher quantities of acid and send the liquor to flotation clarifiers then may or may not filter the clarified liquor. At C and H we converted over to all clarifiers in 1972 and increased our color removal from a range of 15 - 20% to 25 - 35%. We do not pressure filter the Clarified Raw Liquor, sending it directly to char and relying on turbidity instruments to monitor clarity.

For an excellent coverage of the chemistry and effectiveness of phosphatation and carbonation one should read the paper on this subject presented by M. C. Bennett at the 1972 Technical Session of the Cane Sugar Refining Research Project.

4. TALOFLOC PROCESS

Closely tied to the phosphatation process is the Talofloc process, a patented development by Tate & Lyle. This process has been described in papers presented at S.I.T. meetings in 1971 by M. C. Bennett and in 1973 by Rundell, Rich and Norcott. This process has had a good deal of success with some refineries reporting up to 60% color removal with the combination of phosphatation, Talofloc and T & L Clarifiers (papers presented at S.I.T. in 1977 by Barton of Atlantic Sugar and in 1978 by Simoneaux of Supreme Sugar). However each refinery must evaluate the economic potential of the process for its own conditions. With our current level of color removal with phosphatation and our clarifiers at C and H we could not justify the Talofloc process for the additional decolorization we would get.

5. CRYSTALLIZATION

Crystallization is of course a major purification step in the refinery and by the same token achieves significant decolorization. The crystallized sugar is usually only 10% ± 5% of the color of the liquor from which it is boiled. A good part of this remaining color is in the film around the crystal and if we improve crystal quality to have less conglomerates we will have better colors.

At Redpath refinery in Montreal 30 years ago sodium hydrosulfite used to be used occasionally by direct addition to the pan to provide some decolorization. However it didn't seem to produce a lasting effect in the overall color of the granulated sugar because the syrup from the pan became darker in color and subsequent strikes had to be boiled from this dark syrup so the practice was abandoned. I don't know whether any refinery is using hydrosulfite in this way today.

6. OTHER COLOR REMOVAL ADDITIVES

Dr. R. Riffer of the C and H Research Department is presenting a paper at this meeting on laboratory testing of several color removal additives. Some of these look quite interesting and although no one agent looks like a panacea for decolorization we expect to do some further work with two or three of the most promising agents.

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IMPERIAL'S EXPERIENCES WITH GRANULAR CARBON

Thomas N. Pearson

Imperial Sugar Company

In the mid 1970's, it was realized that the decolorization system at Imperial would have to be expanded if we were to maintain the desired granulated sugar colors. This system consisted of phosphatation clarifiers and a bone char house containing thirty 1200 cubic foot char cisterns. This char house was built in 1925 when the melt was less than two million pounds per day. The present melt rate is 3.5 million pounds per day.

After considering other decolorizing systems, including expansion of the present bone char house, the decision was made to proceed with the construction of a granular carbon facility.

Some factors considered in arriving at this decision were:

1. A reduction in BOD of the char waste water due to a reduction of 36% in the burnrate of bone char.

2. No disposal problems as would be encountered with carbonatation or ion exchange.

3. Less dependence on bone char, of which the domestic supply was becoming uncertain.

In December, 1977, the carbon house was put on stream. There are 10 adsorbers, 12 feet in diameter and 31 feet on the straight side, each capable of holding 92,000 pounds of carbon. Normal operation is to run four pairs of adsorbers on liquor, one sweetening off and the other filling. The spent carbon is hydraulically transferred from the adsorber to a spent tank large enough to hold 1½ adsorbers. The carbon is fed to the furnace through a volumetric feeder. In this way precise control of the feedrate can be maintained. The furnace has six

hearths, including an afterburner on the top hearth. It is rated at 42,000 pounds per day. The carbon exits the furnace into a quench tank and is transported by a blowcase to the reactivated tank, which holds 1½ adsorbers. From this tank the carbon slurry, aided by the addition of motive water, flows over a DSM wedge bar screen with a 0.012" opening equivalent to 50 mesh. Most of the fines are removed at this point.

The path of liquor flow was originally through the clarifiers, press filtration, then a double pass over granular carbon and a single pass over bone char.

The initial results were up to our expectations of low color granulated sugar being produced. After several months, when all adsorbers were filled and on stream, we began to experience problems with a gradual drop in flowrate after an adsorber had been on stream for a week or more. Eventually, this flowrate would drop from 115 gpm to as low as 40 gpm. The first reaction was to go from double pass to single pass in an effort to maintain the melt rate. Backwashing of the adsorbers resulted in temporary relief, but an overabundance of sweetwater was produced.

Much speculation took place as to the cause of the pressure drop. Was it a build-up of fines in the carbon bed, air pockets, blockage of the underdrains, filter aid on the surface, or some other unknown cause? The filter station sediment pads did not indicate an abnormal problem and were no different than when we were gravity flowing over bone char. The underdrains were checked and found to be clean. Pressure taps were taken at levels of 3, 10, and 20 feet below the surface of the carbon. This showed that the pressure drop was occurring within the first three feet of the column. Samples were taken from the surface of an adsorber and examined. Filter aid was found to be the cause of the high pressure drop and low flowrate. Even though the sediment tests normally showed no bleed through, we occasionally got shots or might have a bad leaf which was allowed to run too long. Since an adsorber is running 2 to 3 times faster than a char filter and stays on stream for eight weeks, it cannot tolerate even small quantities of filter aid bleed through.

It was decided to change the pattern of flow to go over char first, then over granular carbon. In this way the bone char functions as a prefilter. We have been operating this way since December, 1978, and have not experienced this type of flow problem again.

Decolorization over carbon has averaged 84% for the first eight months of this year. The average color on was 596 and average off was 95. The pH averaged 7.9 on and 7.0 off.

The color was determined by reading the sample as is and calculated as 1000 (-log Ts (420)). The pH going on carbon is adjusted to 8.0 by the addition of a 20% caustic solution.

A pH meter controls a variable speed-proportioning pump which supplies the caustic solution. This system has proven to be very reliable. Good pH control is essential with granular carbon. Even though we are using Cane Cal, which has a built-in pH buffer, a drop of 0.9 to 1.0 pH units is normal. If the pH is not controlled within close limits of 8.0, substantial inversion losses will occur.

After about one year of operating time, we noticed a gradual trend of lower pH liquors off carbon. An investigation revealed that we were losing magnesite through our DSM screen, which screens the carbon slurry before filling an adsorber. The attrition of carbon in the conveying system was causing a loss of magnesite. Two things were done: first, a finer mesh screen was installed and, second, make-up magnesite was added to each adsorber to bring the magnesite level up to 4-5%. Having done this, the pH of the effluent liquors returned to normal. We continue to add about 100 pounds of magnesite to each regeneration.

One adsorber is sweetened off each week, producing about 7800 cubic feet of sweetwater until it reaches one brix. This sweetwater is used for melting washed raw sugar.

As a result of the granular carbon installation, we have reduced our bone char burnrate 36% and eliminated one shift of dumping char filters, which amounts to two men.

With the low level of color off carbon, one would expect that we would never have problems in producing a granulated sugar of very low color; however, this is not always the case. The shift superintendents have been heard to say that, "Previously, we could have produced 35 RBU color sugar with a 200 first liquor, but today we, at times, are having trouble doing it with 110 first liquor color".

Obviously, crystallization is an adjunct color removal system, and different amounts and types of colorants are retained in the sugar crystal which may not have a linear relationship to the first liquor color. We have to address ourselves not only to total color but also with specific colorants. With the wide variety of raws which we have to process, we have to employ supplementary decolorization systems to the old bone char standard. This is an expensive solution to the problem but is the only one at hand now. Perhaps in the near future we will be able to identify the particular colorants in a raw sugar that are not removed by the decolorizing system in use and be able to remove them through other less expensive systems.

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CSR EXPERIENCE WITH ION EXCHANGE RESIN DECOLOURISATION

Howard R. Delaney

CSR Limited

INTRODUCTION

CSR Limited operates an anion exchange decolourisation plant as the sole decolouriser at its Adelaide refinery in South Australia. The process follows affination and carbonation and the decolourised material is boiled directly into white sugar. The plant treats 1500 (dry) tonnes of raw sugar per week and consists of three pairs of columns with each pair operated in series. The resin is regenerated with 10 percent sodium chloride which is fed to the top of the trailing column first and then downflow through the leading column.

The resins used have a strong base quarternary trimethyl-benzyl ammonium exchange site with a copolymer of styrene and divinylbenzene as a support. The resin currently used is a macroporous type and is introduced into the trailing column first and then eventually moved forward to the leading column position.

Rapid deterioration in the decolourisation performance of the ion exchange resin resulting from both an inactivation of the resin functional groups by non-removable ions and blocking of the resin pores by polymerised colourants caused concern.

Research was directed at both these fouling mechanisms and methods of minimising the effects were found. The work also enabled us to explain some of the other observed phenomena associated with ion exchange resin decolourisation.

SELECTIVITY OF COLOUR REMOVAL BY ION EXCHANGE RESINS

Our colourant research had found that over 80 percent of the feed colour to the colourisation process, in its fully ionised state, consisted of flavonoid plant pigments with

the dominant species being the tricin fraction. These tricin derivatives were readily removed by ion exchange resins leaving the decolourised liquor containing mainly luteolin and apigenin derivatives. All these flavonoid pigments have a high anionic charge density and therefore are more readily removed than factory produced melanoidins.

Laboratory work demonstrated that a feed liquor at approximately 9 pH was optimum for decolourisation. At this pH all colourants would be in a negatively charged ionised state and would be available for ion exchange. This effect could not be detected by factory trials over a limited pH range and this was thought to be due to the effect not being significant enough to overcome normal factory variations. Operation at high pH had the disadvantage of increasing the natural pH of the white sugar produced which inflated the measured colour at its solution pH.

The observed efficiencies of decolourisation and regeneration indicated that approximately 10 percent of the resin ion exchange capacity was actively involved in decolourisation, this was most probably on the surface of the bead. There is thus ample time within the bead for polmerization of colourants to occur.

This polymeric structure can be disrupted by exposing the bead to hydrolytic conditions which can break sensitive bonds. Therefore the pH of the brine is important in regeneration and there appears to exist an optimum ratio of chloride and hydroxide ions. In our conditions we have found this to occur at approximately pH 12. Most colourants are attached more strongly than chloride ions and therefore excess chloride (10% NaCl) is used to shift the equilibrium.

In regeneration, tricin based pigments and certain factory produced colourants are more efficiently desorbed than luteolin and apigenin based pigments and phenolic acids. Some of these polymeric structures and irreversibly adsorbed colourants can be broken up and removed by acid washes. The tertiary ammonium groups of the ion exchange resin have the potential for forming stable addition complexes with phenolic compounds which have two adjacent hydroxyl groups. Acid treatment frees the site from these phenolic compounds.

Acid washes have thus been found to be a very effective way of reducing the short term drop in decolourising efficiency caused by irreversibly adsorbed colourants.

Phenolic acids and amino nitrogen compounds, both being colour precursors, were found to be removed to a lesser extent by ion exchange resins than in bone char decolourisation. The phenolic acids react with iron and the

amino nitrogen compounds take part in the Maillard reaction which results in resin decolourised liquors being potentially less thermally stable to colour formation.

Measurements in the refinery using ion exchange resin decolourisation found higher colour formation during crystallization compared with refineries using bone char. This lead to the sugars from the second and third strikes having significantly higher colours than normal.

THE EFFECT OF INORGANIC IONS

Analysis of service resins found that the cations calcium, magnesium, iron and copper and the anions carbonate, silicate, sulphate and phosphate were the most common contaminants of the ion exchange resin.

Our research had shown the deleterious effect of sulphate, silicate, magnesium and calcium on the decolorisation performance of the resin. Iron and copper which are very reactive were known to form highly coloured complexes with colourants and with the resin active groups.

By factory measurements raw sugar was found to be the source of the iron and sulphate. Calcium, magnesium, carbonate and silicate were found to be from the same source as well as from the lime used for carbonatation and the brine regenerant. Copper appeared to originate from the construction materials of the plant itself.

A large proportion of the iron was found attached to the resin by an ion exchange mechanism and could be effectively removed by acid washes.

Particulate matter contamination of the resin, either from the liquor feed or the regenerant proved to be very detrimental.

Very close control of carbonation was required in the factory to minimise soluble calcium fed to the resin. In conjunction with this, filtration performance was upgraded to minimise the release of particulate matter. The quality of the brine was closely monitored for silica and the brine clarification improved to remove the maximum amount of magnesium. Softened water was also used throughout the decolourisation plant area.

The lack of ash removal of the ion exchange resin at times caused increased turbidity to occur in lower grade syrups. The occurrence was usually associated with poor carbonatation performance. The turbidity forming particles were composed of calcium carbonate and silica compounds.

In some of our refineries there is a need to decolourise lower grade syrups for the manufacture of some speciality products. Laboratory trials with ion exchange resins have shown low degrees of colour removal. This poor decolourisation performance is attributed to the increased competition of ash constituents for the ion exchange resins' active sites.

CONCLUSION

Colour removal by anion exchange resins appears to be a combination of ion exchange, adsorption and polmerisation of colourants into the secondary structure of the resin matrix. Effective regeneration therefore requires excess chloride ions and hydrolytic conditions to release adsorbed colourants. Alkaline brine and intermittant acid washes are an effective way of achieving these conditions. The decolourisation performance of an ion exchange resin depends on having the colourant molecules in an ionised state optimal for exchange. In our sugars this is about 9 pH.

Due to the lower amounts of phenolic acid and amino nitrogen compounds removed, resin decolourised liquors have a higher colour formation during crystallization than do char liquors.

Many inorganic anions and cations have a detrmental effect on ion exchange resin decolourisation as they compete with colourants for the resin active sites. The contact of ion exchange resin with inorganic anions and cations must be minimised. This can be achieved by good upstream process control and adequate treatment of the brine regenerant.

The competition of ash with colourants limits the effective use of ion exchange resins for use on lower grade high ash materials.

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Symposium.--Experiences in decolorization alternatives

PRACTICAL ASPECTS OF CHANGING FROM CHAR TO RESIN AT HULETTS

Mike Cox

Huletts Research & Development

INTRODUCTION

Huletts Sugar Refinery in Durban, South Africa, is a 2 000 metric ton per day factory, which originally used bone char for decolourisation. In November 1978 an ion-exchange decolourising plant was commissioned, and has been the sole means of colour removal since.

The processing system at present is :

Melting of VHP raw sugars

Carbonatation

Ion-exchange decolourisation

White sugar boiling

One or two recovery boilings (sugar remelted)

Manufacture of High Test Molasses

The ion-exchange plant consists of 4 vessels in parallel, each containing 12,5 m^3 Amberlite SDC 301 resin. Operating cycles are 18 hours with a 6 hour regeneration time; the flow rate during decolourisation is 3 BV per hour. At any time there are 3 vessels operating with the fourth being regenerated.

Regeneration is accomplished using a 10% brine solution with 0,4% added caustic soda. Every 20 cycles a 4% hydrochloric acid wash is given to remove accumulations of lime and scale.

REASONS FOR CHANGE

The bone char plant was old and in need of extensive repairs

and modifications, which would have been far in excess of the capital cost of the ion-exchange plant.

Labour reductions of the order of 75% were obtained. The small size of the ion-exchange plant can be realised when it is considered that 56 char cisterns have been replaced by 4 resin vessels and a stock of 1 600 tons of char by 50 tons of resin. The ancillary equipment for regenerating the char i.e. conveyors, bucket elevators, kilns, screens, decarbonisers and storage bins also fell away.

A fairly major saving in steam was made by using a single decolourising pass. To achieve acceptable sugar colours with bone char it was necessary to brix down the syrup from the second boiling, rechar, and return to the pans. The additional decolourising power of the ion-exchange plant eliminates this.

Finally, the char plant with large quantities of fairly low brix material was a serious source of microbiological contamination, especially over shut-downs. The very much smaller stock and cleaner conditions of the resin plant have cured this problem to a large extent.

PROBLEMS

Initially when ion-exchange was under consideration there were several unknowns and possible problem areas to be studied.

Resin life under operating conditions

Regeneration procedures

Decolourising performance

Behaviour of Resin treated liquors in panboiling

Effluent disposal

After visiting some operating ion-exchange plants in S.E. Asia to gain first hand knowledge of systems in use, a single column pilot plant was built with a resin volume of 10 litres. This proved invaluable in providing answers to the above points.

Later, at the same time as the main plant was commissioned a more sophisticated 4 column plant was constructed and, this is still in use.

Resin Life and Performance

The first pilot plant was run for over a year. The most

important information obtained was that we could expect a life of roughly 300 cycles at an average decolourisation of 60%.

Figure 1 shows the performance of the first charge of resin in the main plant plotted on 10 cycle average. It indicates that the life and performance of the resin was somewhat better than in the pilot plant, probably due to more constant operating conditions.

The points A, B and C show where the resin was progressively removed from service, one vessel at a time.

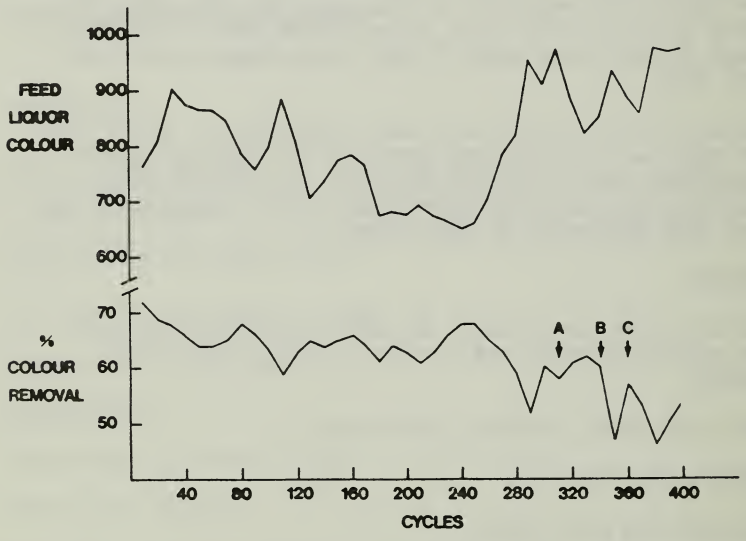

Figure 1.--Feed liquor colours and % colour removal of 1st charge of resin

Percentage decolourisation gives a fair indication of resin performance, but not of the work done by the resin. This is due to the varying feed colours, throughput rates and any by-passing of the resin plant. To overcome this "total colour" loadings were plotted against "total colour" removal. "Total colour" is ICUMSA colour units multiplied by tons per hour through the resin plant.

Figure 2.--Total colour loadings and removals of 1st resin charge

The correlation between colour loading and colour removal is shown in Figure 3.

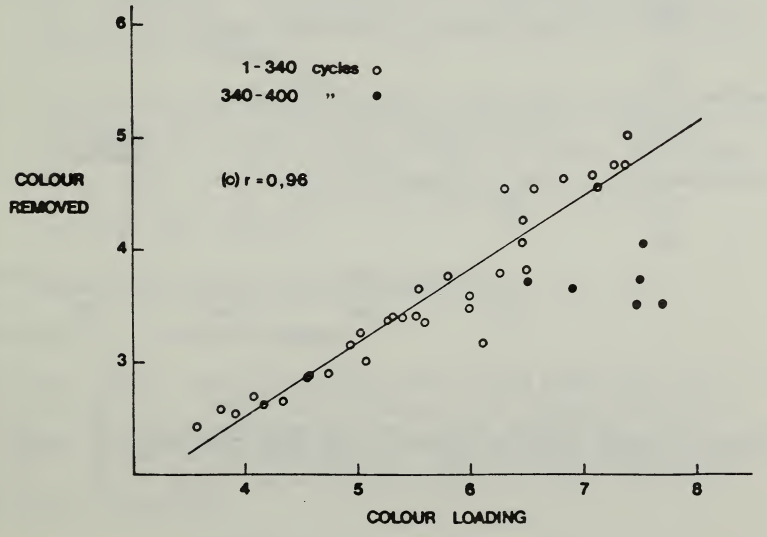

Figure 3.--Correlation between colour loading and colour removal

For most of the resin's working life there is a very strong correlation between colour loading and colour removal. Over the last 60 cycles performance has dropped due to fouling.

During this period there were no low colour loadings and thus we cannot say if the lower performance would have been as noticeable with lower feed colours.

Behaviour of Resin Treated Liquors in Panboiling

The pilot plant supplied treated liquor which was used to simulate factory boilings in the laboratory. A parallel set of boilings from bone char treated liquor was the control.

The lower colours from resin led to the proposal to drop secondary decolourisation between the 2nd and 3rd boilings. Results from before and after the use of resin have borne this decision out. The final Refined Sugar is a blend of all boilings in the ratio 8 : 4 : 2 : 1.

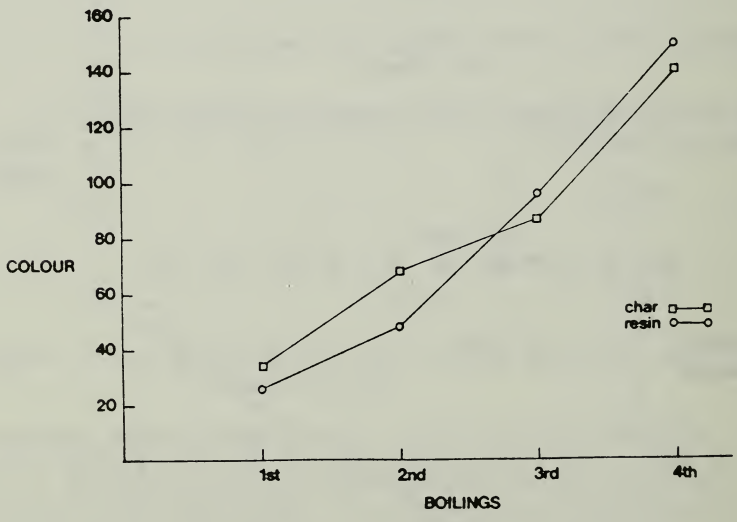

Figure 4.--Sugar boiling colours from bone char and I.E. resin

The comparison between final sugar blend colours calculated from the graph and those actually obtained is :

Decolourisation	Calculated	Actual
Char	57	54
Resin	49	51

Effluent

Effluent disposal was and still is the major problem associated with ion-exchange. Effluent from the pilot plant was used to study treatment methods, and, as no total solution has been found this investigation is still proceeding.

At present our effluent is tankered to a disposal sump controlled by the Municipal Water Department. It is pumped with various other harmless, but difficult to treat effluents 2 km out to sea. Fears that this facility may be barred to us have prompted the continuing work on effluent treatment.

Methods tried have been :

1. Oxidation with sodium and calcium hypochlorite as well as chlorine gas, all proving inefficient and prohibitively expensive.

2. Ozone showed initial promise, but incomplete oxidation was a problem. Recombination of broken down organics back into coloured compounds occurred and very little COD removal was obtained.

3. Ultrafiltration/Reverse Osmosis is the most effective treatment and is still under investigation. Its main advantage is recovery of 80% of the salt used in regeneration with a very high COD removal (± 90%). One drawback is disposal of the small volume of very concentrated effluent that remains.

PROBLEMS ENCOUNTERED AFTER COMMISSIONING

Materials of Construction

Natural rubber and polypropylene were found unsuitable for the inside of a vessel where pressures and temperatures are high. Suitable replacements were butyl rubber for lining the vessel and 316 stainless steel for the distribution pipework. Monel metal was more resistance to attack but exorbitantly expensive.

Regeneration Techniques

Leakage of acidity with subsequent increases in reducing sugar levels after acid washing was cured by giving a normal brine regeneration containing 3,5% caustic soda immediately after the acid wash.

Clumping of the resin sometimes occurs after acid washing, Primal ASE 60 is used to rectify this. Inefficient removal of resin fines and precipitated lime during backwashing has been greatly improved by air injection into the bed.

FUTURE WORK

At present efforts are being concentrated in three main areas. Apart from effluent disposal, they are :

New resin testing;

Rejuvenating fouled resins;

Using exhausted resin as a pre-treatment.

New Resin Testing and Cleaning Fouled Resin

This work is carried out in the 4 column pilot plant where the different resins are tested against each other under identical conditions. The feed liquor, cycle times and regeneration procedures mirror those of the main plant. This type of testing is very time consuming but when the price of resin is considered, it is very worthwhile.

Some results obtained to date are shown in Figures 5 and 6 bearing in mind that results obtained in pilot scale work are usually inferior to those of full scale performance.

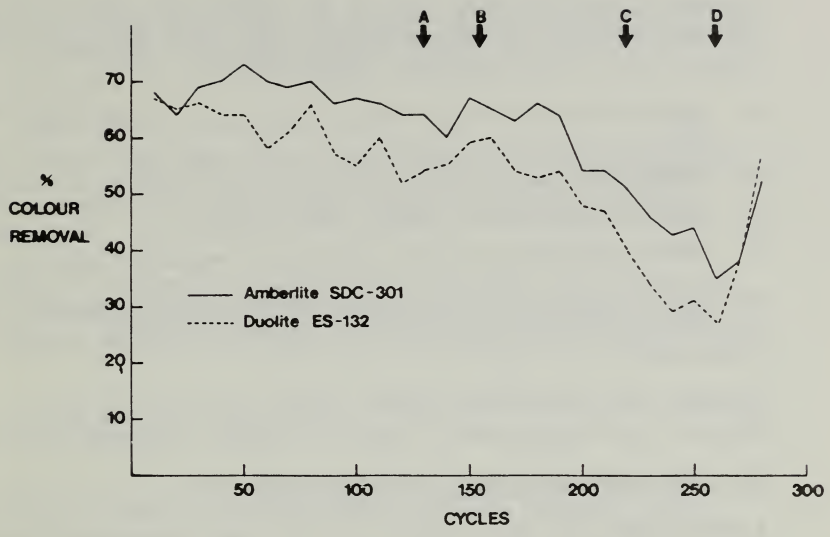

Figure 5.--Performance of Amberlite SDC 301 and Duolite ES 132

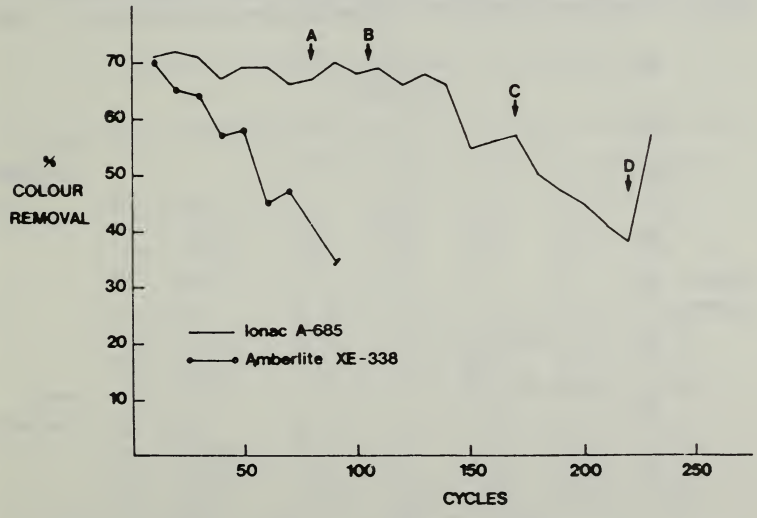

Figure 6.--Performance of Ionac A685 and Amberlite XE 338

With the exception of XE 338, all the above are acrylic resins, SDC 301 and A685 being macroporous and ES 132 a gel type. Points A, B, C and D indicate respectively :

A started the use of 0,2% caustic soda in the brine solution

B stopped the use of caustic soda

C restarted the use of caustic soda (0,4%)

D sodium hypochlorite wash, 6BV with 2% available chlorine

The sodium hypochlorite wash appears very effective but how long the improved performance will last still remains to be established.

Styrene resins have been tested, but not one has been found that will give more than 40 cycles of useful service.

Use of Exhausted Resin as a Pre-treatment

A pilot plant with two columns in series was constructed. Exhaused resin was placed in the first column and new SDC 301 in the second. In operation the feed material passes through the old resin first, whilst in regeneration the flow is reversed. No additional regenerants are used, the first column being regenerated with used brine from the second column. Results as shown in Figure 7 have been very promising to date.

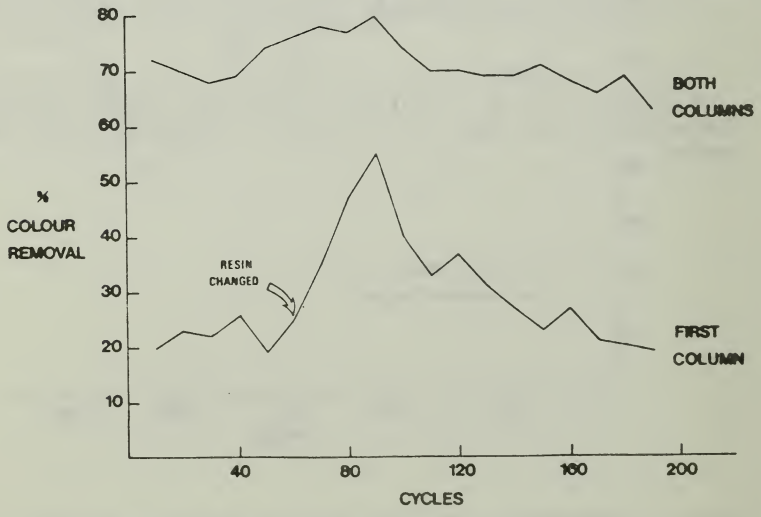

Figure 7.--Performance of SDC 301 in series configuration

Resin changed shows where the original exhausted resin from the first pilot plant was replaced with resin removed from the main plant after 350 cycles.

CONCLUSIONS

The change from bone char to ion-exchange decolourisation at Huletts Refineries, has been a very successful operation. Costs of processing have been reduced and quality of sugar maintained.

Methods of optimising regeneration techniques and finding the most suitable configuration for the use of resins are being studied. Effluent treatment remains a pressing problem.

ACKNOWLEDGMENTS

I would like to thank the staff of Huletts Refinery for the assistance given to me in obtaining all the necessary data for this paper.

APPENDIX

Some of the more important factory analytical data for the seasons before and after changing to resin are set out in Table 1. The change was midway in the 1978/79 season.

Table 1.--Factory analyses for the past 5 Seasons

Season		75/76	76/77	77/78	78/79	79/80
Colour @ 420 nm	Raw Sugar	-	1219	1232	1290	1224
	Brown liquor	850	802	809	785	771
	Fine liquor	450	427	436	350	347
	Ref. Sugar	49	58	54	50	51
Ash	Raw Sugar	0,13	0,14	0,15	0,15	0,15
	Brown liquor	0,23	0,18	0,17	0,19	0,20
	Fine liquor	0,22	0,17	0,15	0,18	0,20
	Ref. Sugar	0,010	0,010	0,010	0,009	0,010
R/S	Raw Sugar	0,12	0,14	0,13	0,14	0,13
	Brown liquor	0,20	0,17	0,16	0,13	0,14
	Fine liquor	0,21	0,15	0,20	0,20	0,15
	Ref. Sugar	0,008	0,009	0,012	0,010	0,006

DISCUSSION AFTER SYMPOSIUM

C. C. CHOU: As Mr. Pearson discussed, the types and structures of colorants do effect the refinery performance to different degrees. I agree with him that we need to identify specific colorants. Currently when we measure color, we not only do not identify the type and structure of colorants, we also still argue about the wavelength to use for color measurement, e.g. 420 nm or 560 nm. However that does not prevent us from using the color measurement as an indispensible tool for process and product quality control purposes. The important thing is to establish the color level of a process stream and/or a product and then to correlate that to the refinery performance. This is what we would like to do with dextran measurements in raw sugar.

M. A. CLARKE: The main reason that we are building a model pan is to study the inclusion of individual colorant compounds in the crystal. The question of which colorants go into the crystal and which stay in the syrup in solution is a question we feel is very important. We are looking at this from the point of view both of raw sugar and refined sugar manufacture. Two of our speakers talked specifically about the different types of colorant and the problems they create in process, giving us reassurance that our group's research is in a desirable and necessary direction. Mr. Delaney said phenolics block resin sites. Compounds such as ferulic acid that Mr. Devereux mentioned are phenolics. Because phenolics do block resin sites and are removed only in the initial passes by resin or by any other adsorbent, they are a set of compounds that get into the pan feed liquor. Phenolics are particularly important, therefore, to examine for their inclusion into the sugar crystal. A point here that did not come up in the discussion after the talk about the pan is that ferulic acid forms color very rapidly. We were very surprised to find that sugar that we boiled containing ferulic acid became yellow very quickly - in a day or so. It made a lot of difficulty in measuring the compound because the ferulic acid had decomposed into several other compounds. This again emphasizes the importance of color developing from some of these individual compounds that we havn't thought very much about - other than as general classes - up to this time.

The color development in boiling changes when you switch from

bone char to resin because you have changed the compounds that have been taken out and changed the types and amounts of color precursors that have been left in the pan liquor, which may develop into colored compounds in the pan.

F. G. CARPENTER (Southern Regional Lab.): As the international referee on sugar color for ICUMSA, I would like to note that at the last meeting in 1978, I finally got world wide agreement that the wavelength will be 420 nm. 560 is now on the way out and should be promptly abandoned if you have not already done so.

K. R. HANSON (Amstar): We still have a large body of customers in the U.S. that are half beknighted in measuring color. They read at 420, but they do take a 720 correction.

F. G. CARPENTER: I would like to take issue with Mr. Delaney on the pH for the color measurement. He said that the color is measured at the existing pH. Although this has been in the ICUMSA methods, this is wrong. What is the purpose of the color measurement? In the processing of sugar, the object is to remove minor constituents, including colorants. So, the object of the color measurement is to indicate the amount of colorant material. Since some of the colorants are indicators, that is, their color changes with pH, it follows that the pH must be kept constant if the color is a measure of the amount of colorant. The same applies to wavelength, as we just noted. Also since the optical measurement detects turbidity, which is always present in sugars, and turbidity depends upon refractive index of the solution, this too must be kept at the standard value. So the color as measured by any device is dependent firstly upon the amount of colorant material, but also depends upon pH, wavelength, and refractive index. Any measurement in which the pH, wavelength and refractive index are not kept at the standard value is confounded, ambiguous, and is not worth anything.

H. R. DELANEY: We are measuring color by the ICUMSA Method which states the natural pH. However, I agree with you that we should be using the standard pH. However, we follow the ICUMSA Method because as our customers redissolve the sugar, they see our sugar color at the natural pH.

F. G. CARPENTER: Mr. Delaney noted that for ion exchange to be an effective decolorizer, the colorant had to be ionized which required pH 9. At this pH color is also being formed.

H. R. DELANEY: Color formation at pH 9 comes mostly from alkaline degradation of reducing sugars, so the way we minimize this is to go for very very low reducing sugar contents by affination. Our work indicates that we are not getting significant amounts of color formation.

F. G. CARPENTER: I believe that it is incorrect to emphasize color removal in clarifiers. What are clarifiers for? They are to remove particulate matter. They should be conceived, designed, operated, and controlled to remove particulate matter. They should be appraised in terms of clarity of effluent and any incidental color removal only mentioned in passing. The only reason any color was removed was because the color was associated with particles that the clarifier caught.

R. KUNIN: I disagree. If we could make a precoat filter that removed all the particles and color at the same time, we would have achieved a fine objective and we would be way ahead in terms of energy, capital investment and operating costs.

R. S. PATTERSON: Mr Cox mentioned that the styrene base resins had not been effective. I wondered whether he had done any laboratory work in South Africa on acrylic base resins in the first position and styrene base resins in the second position.

M. COX: No, we have not done any testing of that combination.

M. MATIC: I think, however, that system does work. The SMRI has investigated that combination.

R. S. PATTERSOM: I have heard that system is used in Brazil.

R. RIFFER: I have worked on the effect of pH on resin decolorization. There is some evidence that phenolic color is better adsorbed at high pH, whereas carboxylic acid color is better adsorbed at low pH.

On the subject of ultrafiltration, I know that these membranes are highly susceptible to fouling. Can Mr. Cox tell us what kind of membranes he used?

M. COX: They are cellulose acetate spiral wound membranes and we have no troubles with fouling. We have run them in a pilot plant for 6 months.

R. KUNIN: Ultrafiltration (UF) is a most useful technique that has been ignored too long. The current membranes in the best ultrafilters can be backflushed and they do not plug as do the reverse osmosis membranes or electrodialysis membranes. They are completely inert, can be operated at very high temperatures, even in sugar syrups. UF does a fantastic job on clarification and removal of some color bodies. I am intrigued with the thought of using UF on waste brine regenerant, however most of the molecular weight cut off's of the ultrafiltration membranes are in the thousands. Does not that limit the usefulness of ultrafiltration in that some colorants will sneak through and tend to build up continuously?

M. COX: The membrane we are using has a cut off of 750. It

is on the borderline between reverse osmosis and ultrafiltration. It requires a fairly high pressure. The manufacturers are so sure of their product that they have given us a guarantee of 1 year on the membranes.

H. R. DELANEY: One of the problems in the reuse of regenerant is that there are inorganic ions that build up, especially sulfate which is detrimental to resin. This could start limiting this system. The way around is, of course, to use a fairly large bleed and dump the system entirely every so many cycles.

K. R. HANSON: Those of you who have abandoned or are contemplating abondoning bone char for ion exchange, all operate with highly desirable raws. Let me pose a question to you. Suppose you have to run for weeks on end with raws of 97.5 to 97.7 pol, color value 2.5 to 3 times your present level and make only limited amounts of soft sugars. These factors dictate you must operate an extensive recovery system. Would you prefer bone char or ion exchange?

R. S. PATTERSON: We don't have the problem because our Hawaiian raws have improved to 98.8 pol and color of washed raw sugar is less than 1000. But, I would still tend to stay with bone char for low purity, dark colored raws.

H. R. DELANEY: The ion exchange resins have an enormous capacity for color but they suffer from the adsorption isotherm being flatter than that of bone char. This means that the effluent color reflects an increase in feed color rather more than it would with bone char. This means that with heavy color loads on ion exchange resins you will be in real trouble. You better stay with bone char for heavy color loads. The resins should be used up front to take advantage of their high capacity and then use something else after them.

R. KUNIN: The point about isotherms with respect to carbon vs resin is very important. You can prepare interesting precoats with carbonaceous material as well as with resin. A combination of materials can be worked together optimizing particle size and pressure drop and hopefully can take on a heavy color load in a precoat, thereby minimizing capital investment and waste disposal.

M. COX: I think you should do what we did in South Africa; make your raw sugar suppliers give you a decent product.

A. JAMES (Consultant): About 12 years ago at SIT, Arthur Moult read a paper about the new granular carbon plant at Liverpool, and he rather shocked the crowd by starting then to talk about the effect on sugar loss. I wonder if anyone has seen any effect on sugar loss of any changes they have made?

T. PEARSON: I don't believe that we have seen a measurable change in sugar loss, but our granular carbon plant is another point of irreversible adsorption and another time delay at high temperature, so I suspect that we are increasing sugar loss.

H. R. DELANEY: Measuring loss is a very delicate operation, but in the first few years of operation of our total ion exchange refinery, we were very excited about the reduction in loss. Unfortunately, after a couple of years the loss started to climb up again. Currently it is on its way down. However, we do feel that the losses are less, primarily because of reduced residence time and there is less chance of microbial action.

M. COX: It is very difficult for us to tell at the moment because making high test molasses makes the whole sugar balance across the refinery almost impossible to calculate. Our yields are very high, like 98.4%. We believe that the losses have been cut significantly.

R. S. PATTERSON: In regard to losses to carbon, the Bone Char Project, Tate and Lyle, and ourselves all measured the irreversible adsorption and found that carbon retains 4 to 10 times as much sugar as bone char per unit of adsorbent, but there is a much longer cycle over carbon, so per unit of sugar processed, the loss to carbon is less than or about the same as bone char.

R. KUNIN: After 25 years we finally have C & H interested in ion exchange. It has been 15 years that my associates and I have been trying to get Hulett's to use ion exchange resins. It has taken close to a generation to get the Australians in this direction. So I should leave this conference pretty happy. But, I feel that many of the problems with ion exchange will be solved with powdered resin technology if the bottom line, as indicated, is in fact correct. Mr. Patterson mentioned that going to powdered ion exchange on a throw away basis is a step backward, but I think that this is a trend that technology is taking in the U.S. We are relearning how to burn coal, We are building cars smaller, and we are getting back to a more reasonable technology that fits within our current requirements. I hope that I will not have to wait another generation before powdered ion exchange technology comes into its own.

M. A. CLARKE: Does anyone have to deal with sugars that have been prepared with sulfitation?

R. S. PATTERSON: One or two factories in Hawaii are now starting to try sulfitation. They are re-inventing the wheel. They probably did it 40 years ago. Now they are trying it again.

M. A. CLARKE: I have some comments on this process, which is, unfortunately, reappearing here and there among raw sugar producers. We had some contact recently with a refinery that was dealing with raw sugars made by sulfitation, and paying a premium for low colors on these raws. It so happened that they didn't know their raw sugar had been made by sulfitation. This was not the old SO_2 process; it was simple addition of sulfite to final syrup. In process, the refinery found that they didn't seem to be removing much color in the clarifier. They thought there was a clarifier problem, but there wasn't. In the raw sugar the sulfite had chemically reduced the colorants to uncolored compounds. When this sugar was melted, the heat and the air in the clarifiers caused oxidation and brought the color back again. So the refinery was not making new color in the clarifiers, they were just recreating the color that they had bought in bleached form in the sugar. The overall effect in the clarifier, as color was being formed, was to show little color reduction over clarification. The overall cost effect of premiums plus additional clarification chemicals and decolorization treatment, was no reduction at all, but rather an increase.

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